R. P. RASTOGI
V. K. SRIVASTAVA

AN INTRODUCTION TO QUANTUM MECHANICS OF CHEMICAL SYSTEMS

AN INTRODUCTION TO QUANTUM MECHANICS OF CHEMICAL SYSTEMS

R.P. RASTOGI
and
V.K. SRIVASTAVA

S.C.E.R.T. West Bengal
Library
Calcutta
25/3, B. C. Road

OXFORD & IBH PUBLISHING CO.
New Delhi Bombay Calcutta

[illegible] LIBRARY
Date 8.7.03
Accn. No. 10696

© 1986 R.P. Rastogi and V.K. Srivastava

ISBN 81-204-0073-9

Published by Mohan Primlani for Oxford & IBH Publishing Co.,
66 Janpath, New Delhi 110 001 and printed at Gidson Printing
Works, C-130, Mayapuri Indl. Area, Phase II, New Delhi 110 064

Preface

The present book covers one common semester course on quantum mechanics for postgraduate students including biology students having poor mathematical background, which the senior author has taught since 1970 in Gorakhpur University. It starts with a background which is familiar to students of Indian Universities as well as, that of other developing countries. In contrast, majority of foreign books are based on the assumption that the readers possessed understanding of specific levels which is not true in the Indian context. Hence, the subject matter has been developed on the basis of a logical structure which is readable and consistent.

The book is intended to be an introductory text for postgraduate level for Indian Universities and not a monograph. However, a comprehensive treatment of areas in chemistry where the impact of quantum mechanics is profound has been included in the text. Mathematical details have been avoided but concept has been emphasised.

The subject matter has been divided into fifteen chapters. The first three chapters deal with the foundations of quantum mechanics. The subject matter of the following chapters has been divided into the following groups:

1. System having free electrons
2. System having atoms with bound electrons
    - i) Simple atoms—one electron system
    - ii) Polyelectronic atoms
3. Small molecules
4. Large organic moles
5. Complex inorganic compounds
6. Weak interactions
7. Behaviour of group of atoms and molecules.

A chapter on symmetry of molecules and orbitals has been included in order to familiarise the reader with the use of group theory in solving quantum mechanical problems. A chapter on mathematical techniques used in quantum mechanics has also been included in the end to provide relevant material for the proper appreciation of mathematical steps. Number of useful appendices have been added at the end of the chapters which make the subject-matter more comprehensive. About 80 problems, some of them solved, have been added at the end, and these enhance the utility of the book.

The financial assistance of U.G.C. in the preparation of the manuscript and the help rendered by Dr. Sushma Rastogi is gratefully acknowledged. The authors are grateful to Dr. Kehar Singh and Dr. S.C. Bahel for the help rendered in the early stages. Thanks are due to Dr. M.C. Gupta for critically going through the manuscript in the final stages and the help rendered in writing Chapter 13 and the appendices.

R.P. RASTOGI
V.K. SRIVASTAVA

Contents

Preface iii

Chapter 1 QUANTUM HYPOTHESIS 1
- 1.1 Historical development of quantum theory 1
- 1.2 Black body radiation 11
- 1.3 Photoelectric effect 15
- 1.4 Compton effect 17

Chapter 2 DUAL CHARACTER OF ELECTRON AND UNCERTAINTY PRINCIPLE 20
- 2.1 Dual nature of electron 20
- 2.2 Heisenberg's uncertainty principle 21

Chapter 3 BASIS OF WAVE MECHANICS AND SCHRÖDINGER EQUATION 26
- 3.1 Schrödinger wave equation 26
- 3.2 Significance of ψ-function 29
- 3.3 Solution of the wave equation 32
- 3.4 Approximate solutions of Schrödinger equation 34

Chapter 4 WAVE MECHANICS OF FREE ELECTRONS 37
- 4.1 Free particle in a box 37
- 4.2 Particle in a rectangular three-dimensional box 40
- 4.3 Particle in a ring 42
- 4.4 Particle on the surface of a sphere 46
- 4.5 Applications of the free-electron model to chemical systems 48
- Appendix I: Tunnel effect 50
- Appendix II: Free-electron moving in a periodic potential 52

Chapter 5 WAVE MECHANICS OF BOUND ELECTRONS—ONE ELECTRON SYSTEM (HYDROGEN ATOM AND HYDROGEN ATOM LIKE IONS) 53
5.1 A simple solution of Schrödinger equation for hydrogen atom 54
5.2 Generalised solution of Schrödinger equation 56
5.3 Pictorial interpretation of wave-functions 62
5.4 Contour diagrams 64
5.5 Three-dimensional plots 67
5.6 Bohr's theory and Schrödinger equation 67

Chapter 6 POLYELECTRONIC ATOMS 68
6.1 Helium atom 68
6.2 Perturbation method 69
6.3 Variation method 71
6.4 Elements other than hydrogen and helium 73
6.5 Hartree self-consistent field method 75
6.6 Energy states of hydrogen-like atoms and polyelectronic atoms 77

Chapter 7 SMALL MOLECULES 78
7.1 Hydrogen molecule ion 78
7.2 Evaluation of E 79
7.3 Evaluation of ψ and ψ^2 82
7.4 Comparison of theory and experiment 84
7.5 Excited states of H_2^+ 86
7.6 Hydrogen molecule 87
7.7 An alternative wave-function—V.B. treatment 89
7.8 Comparison of V.B. and M.O. wave-functions 92
7.9 Further refinements 92
7.10 Chemical bonding 92
7.11 Spin pairing and chemical bond 94
7.12 Energy of molecular orbitals 96

Chapter 8 SMALL INORGANIC MOLECULES 98
8.1 Homonuclear diatomic molecules 98
8.2 Heteronuclear diatomic molecules 100
8.3 Polyatomic inorganic molecules 102
8.4 Hybrid orbitals 105
Appendix: Electron repulsion theory 109

Chapter 9 SYMMETRY OF MOLECULES AND ORBITALS 111
9.1 Symmetry of molecules 111

9.2 Group theory 114
9.3 Symmetry operation of orbitals 116
9.4 Application of group theory to simple molecules 117

Chapter 10 LARGE ORGANIC MOLECULES 120
10.1 Ethylene 121
10.2 Butadiene 125
10.3 Benzene 131
10.4 Electron density 136
10.5 Bond order 139
10.6 Free valence 142
10.7 Molecular orbital treatment of naphthalene 143
Appendix I: Approximate methods in M.O. theory of large molecules 147
Appendix II: Generalised treatment of Simple Hückel Molecular Orbital theory (SHMO) 151

Chapter 11 COMPLEX INORGANIC COMPOUNDS 156
11.1 Electrostatic theory 157
11.2 Crystal field theory 157
11.3 Valence bond theory 158
11.4 M.O. treatment of complex ions 158
11.5 Molecular orbitals of metal ligand bonds 161
11.6 Ligand field theory 163
11.7 Electronic spectra of transition metal complexes 169

Chapter 12 WEAK CHEMICAL INTERACTION 170
12.1 London interaction 170
12.2 Donor acceptor interaction 173
12.3 Hydrogen bonding 175
Appendix: Perturbation theory of van der Waals forces for hydrogen atom 178

Chapter 13 ELEMENTS OF QUANTUM STATISTICS 180
13.1 Quantum effects in kinetic theory 180
13.2 Relationship of quantum mechanics and statistical mechanics 183
13.3 Quantum statistics 185

Chapter 14 MATHEMATICAL TECHNIQUES 188
14.1 Determinant 188

14.2 Matrices 191
14.3 Operator 194
14.4 Functions 196

Chapter 15 ORBITAL SYMMETRY CONSERVATION IN CHEMICAL REACTIONS 198

Problems

General principles of wave mechanics 203
Quantum mechanics of atoms 210
Quantum mechanics of molecules 217
Ligand field theory and intermolecular forces 229

Appendix I: SOME PHYSICAL CONSTANTS AND DEFINED VALUES 232

Appendix II: CONVERSION FACTORS 233

Further Reading 234

Index 237

CHAPTER 1

Quantum Hypothesis

1.1 Historical Development of Quantum Theory

Quantum mechanics or wave-mechanics was developed as a sequel to quantum hypothesis. An idea of the history of this development can be had from Table 1.1.

The seeds of quantum mechanics were laid in the beginning of the 20th century, when a revolutionary idea regarding the nature of energy was suggested. This was necessary since theories based on older concept could not explain certain experimental facts. We shall first briefly outline the earlier concept of energy and discuss how it ran into difficulties.

Earlier ideas about energy were mainly drawn from the kinetic theory of gases, which shows that $PV = 2/3$ K.E. $= RT$. In other words, a simple molecular picture leads to the conclusion that translational energy of a mole of gas is just $3/2\ RT$. Since the movement of molecules can occur along the three axes x, y, and z, the molecules have three translational degrees of freedom. According to the law of equipartition of energy, it is supposed that energy is equally distributed in each degree of freedom and hence each degree of freedom is associated with energy equal to $1/2\ RT$ per mole. The immediate consequence of this concept is that since T can assume any value, $1/2\ RT$ is also a continuous function and hence the energy can vary continuously. The energy of a molecule includes translational, vibrational and rotational energy. Thus, the total energy would then be governed by the

Table 1.1. Outline of historical development of quantum theory

Year	Investigators	Contribution
1900	Planck	Radiation formula through energy quanta
1905	Einstein	Photo-electric effect through photons
1901-13	Einstein, Debye, Born	Specific heats of crystals near absolute zero
1911	Rutherford	Atoms with small positive nucleus
1913	Bohr	Simple model of hydrogen atom
1914	Franck, Hertz	Atomic energy levels by electron bombardment
1915-16	Wilson, Sommerfield	Rules of quantisation
1922	Stern, Gerlach	Discrete values for physical quanta
1923	Compton	Inelastic collision of photons and electron
1924	de Broglie	Wave nature of electron and matter
1925	Pauli	Exclusion principle
1926	Heisenberg, Born, Jordon, Schrödinger	Wave mechanics and Matrix mechanics
1927	Heisenberg	Uncertainty principle
1927	Davisson, Germer	Electron diffraction by crystal
1927	Burren, Heitler, London et al.	Application to hydrogen molecule ion and hydrogen molecule
1930-40	Slater, Kirkwood, Lennard-Jones	Perturbation theory

number of degrees of freedom including rotational and vibrational, each degree of freedom carrying energy equivalent to 1/2 RT per mole or 1/2 kT per molecule where k is the Boltzmann constant.

The above concept of energy based on kinetic theory was a powerful concept and it could explain many unrelated experimental findings. For example, it could be used to predict with success, the ratio of specific heats of gases at constant pressure and at constant volume. However, by the end of 19th century, many experimental results accumulated which could not be explained on the basis of the above concept. Amongst these were the experimental results on the temperature dependence of specific heats of solids (Fig. 1.1) and the line spectrum of hydrogen (Fig. 1.2).

We shall first discuss the results on the specific heats of solids. Figure 1.1 clearly shows that (i) specific heat of diamond strongly

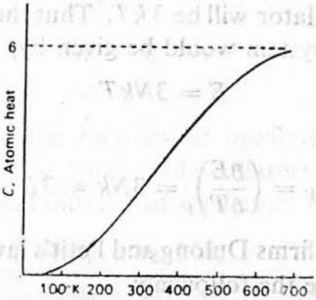


Fig. 1.1. Variation of atomic heat of diamond with temperature.

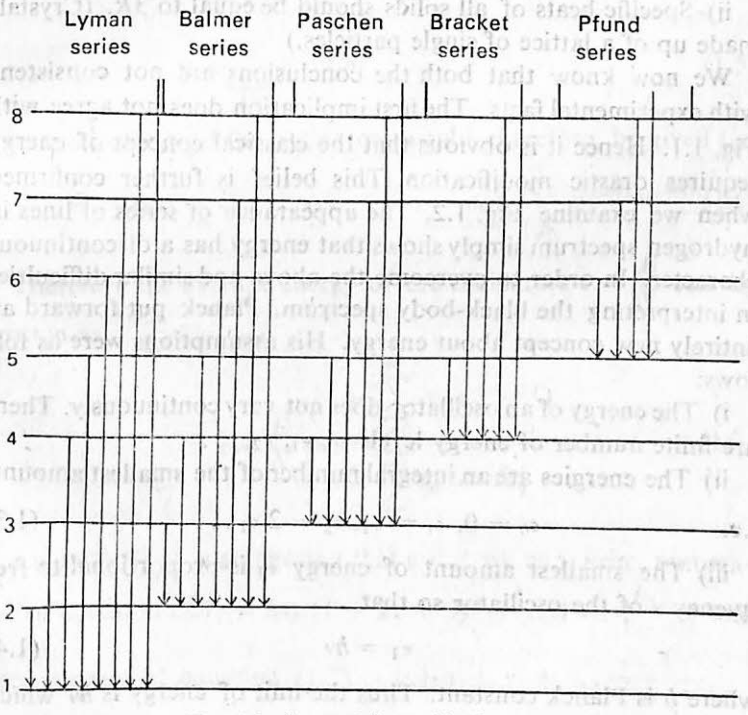


Fig. 1.2. Spectral lines of hydrogen.

depends on temeprature below 1000°C and tends to approach zero at absolute zero and (ii) beyond 1000°C the value approaches 3 R. Let us examine whether the classical energy picture predicts these experimental features. We consider a crystal containing N atoms occupying definite lattice positions. Each atom will be free to oscillate around its mean position along three perpendicular planes. In each plane it will have two degrees of freedom. Hence energy of each oscillator will be $3\,kT$. Thus the total energy E of N oscillator in the system would be given by,

$$E = 3NkT \tag{1.1}$$

and therefore

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk = 3R \tag{1.2}$$

which in a way, confirms Dulong and Petit's law. The implications of equation (1.2) are the following:

i) Specific heat at constant volume is independent of temperature.

ii) Specific heats of all solids should be equal to $3R$. (Crystals made up of a lattice of single particles.)

We now know that both the conclusions are not consistent with experimental facts. The first implication does not agree with Fig. 1.1. Hence it is obvious that the classical concept of energy requires drastic modification. This belief is further confirmed when we examine Fig. 1.2. The appearance of series of lines in hydrogen spectrum simply shows that energy has a discontinuous character. In order to overcome the above and similar difficulties in interpreting the black-body spectrum, Planck put forward an entirely new concept about energy. His assumptions were as follows:

i) The energy of an oscillator does not vary continuously. There are finite number of energy levels $\epsilon_0, \epsilon_1, \epsilon_2, \ldots$

ii) The energies are an integral number of the smallest amount, i.e.

$$\epsilon_0 = 0,\ \epsilon_1 = \epsilon_1,\ \epsilon_2 = 2\,\epsilon_1 \ldots \tag{1.3}$$

iii) The smallest amount of energy ϵ_1 is proportional to frequency ν of the oscillator so that

$$\epsilon_1 = h\nu \tag{1.4}$$

where h is Planck constant. Thus the unit of energy is $h\nu$ which is called quanta.

Planck suggested a method using the above assumptions to calculate the energy of a system containing N oscillators particularly when number of oscillators may occupy different energy levels. This procedure is given below.

According to Boltzmann distribution law we have

$$
\begin{aligned}
n_1 &= n_0\, e^{-\epsilon_1/kT} \\
n_2 &= n_0\, e^{-\epsilon_2/kT} \\
\dots &\quad \dots \quad \dots \\
n_i &= n_0\, e^{-\epsilon_i/kT} \\
\dots &\quad \dots \quad \dots
\end{aligned}
$$

where $n_1, n_2, \dots$ are the number of oscillators having energies $\epsilon_1, \epsilon_2, \dots$ and n_0 is the number of oscillators in the lowest energy state. Hence the total number of oscillators would be given by,

$$
\begin{aligned}
N &= n_0 + n_1 + n_2 + \dots \\
&= n_0 + n_0\, e^{-\epsilon_1/kT} + n_0\, e^{-\epsilon_2/kT} + \dots
\end{aligned}
$$

so that,

$$
\begin{aligned}
N &= n_0\,(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots) \\
&= n_0 \sum_{x=0}^{\infty} e^{-xh\nu/kT} \qquad (1.5)
\end{aligned}
$$

The total energy of the oscillators would, therefore, be given by

$$E = \epsilon_0 n_0 + \epsilon_1 n_1 + \epsilon_2 n_2 + \dots = n_0 h\nu \sum_{x=0}^{\infty} x\, e^{-xh\nu/kT} \qquad (1.6)$$

Therefore the average energy of the oscillators $\bar{\epsilon} = \frac{E}{N}$ can be written as

$$\bar{\epsilon} = \frac{E}{N} = \frac{h\nu \sum_{x=0}^{\infty} x\,(e^{-xh\nu/kT})}{\sum_{x=0}^{x=\infty} (e^{-xh\nu/kT})} \qquad (1.7)$$

Putting $e^{-h\nu/kT} = y$ and noting that $y < 1$ we can write, numerator of equation (1.7) $= h\nu y\,(1 + 2y + 3y^2 + \dots) = \frac{h\nu y}{(1-y)^2}$ and denominator of equation (1.7) $= 1 + y + y^2 + \dots = \frac{1}{1-y}$.

Therefore $$\bar{\epsilon} = \frac{E}{N} = \frac{h\nu y}{1-y} = \frac{h\nu}{e^{h\nu/kT}-1} \tag{1.8}$$

which is the quantum mechanical expression of the average energy of an oscillator.

We shall now try to examine quantitatively the difference between the classical and quantum energy concepts and to see whether the two can be reconciled under specific conditions.

Therefore,

$$\bar{\epsilon} = \frac{E}{N} = \frac{h\nu y}{1-y} = \frac{h\nu}{e^{h\nu/kT}-1} \tag{1.8}$$

We shall now try to examine what is the difference between the classical and quantum energy concepts and whether the two can be reconciled under certain circumstances.

It follows that when,

$$\frac{h\nu}{kT} \ll 1 \quad \text{then} \quad (e^{h\nu/kT}-1) = \frac{h\nu}{kT}$$

so that using equation (1.7) we get $\bar{\epsilon} = kT$ which is the classical value of average energy of an oscillator. Thus, it follows that at high temperature or when the value of ν is low, quantum and classical results may be similar. This is the case for diamond for which the classical theory and quantum theory both yield identical values of specific heats at high temperature $\sim$ 1000°C.

We shall now examine the extent to which quantum hypothesis quantitatively explains the specific heat results at various temperatures.

Using equation (1.8) the total energy E of $3N$ oscillators would be given by;

$$E = 3N\,\frac{h\nu}{e^{h\nu/kT}-1} \tag{1.9}$$

so that c_V, the specific heat at constant volume is given by

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk\,\frac{e^{h\nu/kT}\left(\dfrac{h\nu}{kT}\right)^2}{(e^{h\nu/kT}-1)^2} \tag{1.10}$$

where E denotes the internal energy and V denotes the volume.

Equation (1.9) is called Einstein equation for specific heat of solids. At high temperatures when $\frac{h\nu}{kT}$ is small, c_V would tend to $3R$ according to equation (1.10).

We shall not follow the historical sequence of the phenomena which were quantitatively explained by quantum hypothesis. Instead, we shall discuss the case of hydrogen spectrum and critical potentials since these are more familiar.

In 1886, J.J. Balmer discovered a relationship for the frequencies of the lines in the visible region of the hydrogen spectrum. The wave number $\bar{\nu}$ was found to satisfy the following empirical equation,

$$\frac{1}{\lambda} = \bar{\nu} = R\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1} \qquad (1.11)$$

where $n_2 = 3, 4, 5 \ldots$. The constant R is called Rydberg constant and as the value 109, 677.76 cm^{-1}. Later on some additional series of lines were discovered. Ritz (1908) showed that in genenal the frequency of radiations in such series could be expressed as a difference of two terms, i.e.

$$\frac{1}{\lambda} = \left(\frac{R}{n_1^2} - \frac{R}{n_2^2}\right) \text{cm}^{-1} \qquad (1.12)$$

where the values of n_1 and n_2 are given in Table 1.2.

Table 1.2. Parameters of equation (1.12)

Series	n_1	n_2	Spectral region
Lyman	1	2, 3, 4, . . .	UV
Balmer	2	3, 4, 5, . . .	Visible
Paschen	3	4, 5, 6, . . .	I.R.
Bracket	4	5, 6, 7, . . .	I.R.
Pfund	5	6, 7, 8, . . .	I.R.

The classical energy concept cannot explain the hydrogen spectrum since it predicts a continuous spectrum. In fact, the classical theory predicts that the Rutherford atom would be unstable since an electron moving in a circular path would emit continuous radiation and would lose energy continuously. It would ultimately fall into the nucleus within a period of 10^{-10} sec. But on the contrary the atoms are found to be stable and to emit radiations of certain characteristic frequencies only when excited. Equation

(1.12) was theoretically obtained by Bohr using quantum hypothesis and a particular model of atom. The experimental value of Rydberg constant was found to agree well with the theoretical value. In order to derive equation (1.12) from theoretical considerations, Bohr made the following assumptions:

1) Electrons can revolve around the nucleus only in certain allowed energy states.

2) Radiation is emitted in descrete quanta whenever an electron jumps from a higher energy level E_2 to a lower energy level E_1. The energy change during electron jump is given by

$$\Delta E = E_2 = E_1 = h\nu \tag{1.13}$$

Similarly when radiation is absorbed, energy change would be $E_1 - E_2$.

3) The motion of an electron is restricted in such a manner that angular momentum (mvr) is an integral multiple of $h/2\pi$, i.e.,

$$mvr = \frac{nh}{2\pi} \tag{1.14}$$

thus, the electron is supposed to move in fixed orbits with the nucleus situated at the centre. Using above assumptions and the condition of equivalence of centrifugal force and electrostatic force of attraction we obtain following equations connecting the radius of the orbit r_n, energy E_n and velocity of an electron in a particular orbit n,

$$r_n = \frac{n^2h^2}{4\pi^2 me^2} \tag{1.15}$$

$$E_n = -\frac{2\pi^2 me^4}{n^2h^2} \tag{1.16}$$

$$v_n = \frac{e}{\sqrt{mr}} \tag{1.17}$$

where h is Planck constant, m is mass of an electron and e is the electronic charge. The calculated values of the radius and energy of different orbits are given in Table 1.3. When $n = 1$, r_n is represented by a_0 which is called Bohr radius.

If ν is the frequency of the radiation emitted in the process of electron jump from the orbit n_2 to orbit n_1 we have

$$\Delta E = E_{n_2} - E_{n_1} = h\nu = -\left(\frac{2\pi^2 me^4}{n_2^2\, h^2}\right) - \left(-\frac{2\pi^2 me^4}{n_1^2\, h^2}\right) \tag{1.18}$$

Table 1.3. Radius and energy of different orbits of hydrogen atom

n	$r\ (A^\circ)$	$E\ (\text{cm}^{-1})$	$v\ (\text{cm sec}^{-1})$
1	0.529	−109,700	2.32×10^8
2	2.1	−27,400	—
3	4.8	−12,200	—
4	8.5	−6850	—

ΔE is also called resonance potential. From equation (1.18) we have,

$$h\nu = 2\pi^2 me^4/h^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \tag{1.19}$$

or

$$\frac{1}{\lambda}=\bar{\nu}=\frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

since

$$\nu=\frac{c}{\lambda}=c\bar{\nu}$$

we have,

$$\bar{\nu}=\frac{2\pi^2 me^4}{ch^3}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \tag{1.20}$$

Equations (1.12) and (1.20) are identical in form. Comparing the two equations, we have

$$R=\frac{2\pi^2 me^4}{ch^3} \tag{1.21}$$

When appropriate values of m, e, c and h are substituted on the right hand side of equation (1.21), the calculated value is found to be $1.09679\times10^5\ \text{cm}^{-1}$ which is in good agreement with the experimental value. Such a comparison has given strong support to the concept of stationary energy levels and quantum hypothesis.

Equation (1.18) can be experimentally tested by direct measurement of resonance potential which is a measure of the energy required to raise the electron from a lower to a higher energy level. The energy required to remove an electron to an infinite distance, is called the ionisation potential and this can also be measured directly. The theoretical value of the ionisation potential can be calculated from equation (1.18) by putting $n_2=\propto$.

Experimental measurement of resonance potential is based on the following principle. If an electron collides with the atom of an element (in the vapour state) either of the following events can happen as shown in Fig. 1.3.

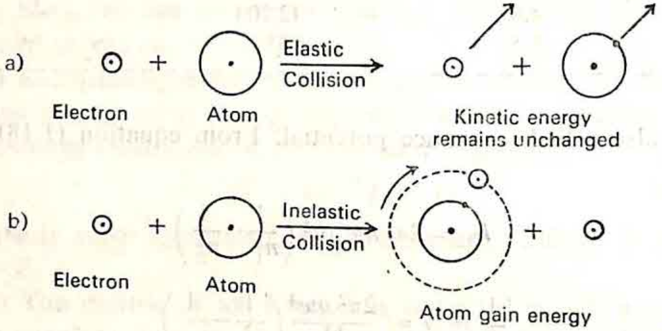


Fig. 1.3. Schematic diagram of collision of an electron with an atom.

a) An elastic collision without affecting the kinetic energy of impinging electron may occur. (b) The kinetic energy may be just sufficient to raise the electron from lower level to a higher energy level so that the impinging electron would lose some of its kinetic energy. Thus, if we have a device to measure the current due to flow of electrons, then in case (a) flow of current would be indicated whereas in case (b) the current would suddenly attain a low value. The kinetic energy of the electrons can be controlled by having an accelerating potential field in the path of the electron beam. The accelerating potential which is just sufficient to bring about the situation (b) would be equal to the resonance potential.

Following techniques have been used for the determination of ionisation potentials.

a) direct photoionisation experiments,
b) ultraviolet Rydberg series measurements,
c) electron impact experiments, and
d) photoelectron spectroscopy.

Techniques (a) and (b) give adiabatic values while it has been claimed that the electron impact experiments yield vertical ionisation potentials. However, it has been pointed out that, although low resolution experiments should yield vertical values high resolution experiments give adiabatic ones. The photoelectron spectroscopy yields, in principle, both adiabatic and vertical values.

If an atom contains more than one electron, there will be first, second, third etc., ionisation potentials. For example, the first ionisation potential of a lithium atom is the energy required for $Li \rightarrow Li^+ + e$; the second ionisation potential is the energy for $Li^+ \rightarrow Li^{2+} + e$.

It is also possible to measure successive ionisation potentials which can be compared with theoretically predicted values based on Bohr model of atom. Values of first and second ionisation potential of a few elements are given in Table 1.4.

Table 1.4. Ionisation potential of some atoms (eV)

Element	First ionisation potential	Second ionisation potential
H	13.60	
He	24.58	54.50
Li	5.39	75.62
Be	9.32	18.21
B	8.30	25.15
C	11.26	24.38
N	14.54	29.60
O	13.62	35.15
F	17.42	34.98
Ne	21.56	41.07

In the subsequent pages we shall discuss a few more independent phenomena which give further support to quantum hypothesis.

1.2 Black Body Radiation

Hot bodies emit radiations similar to electromagnetic radiations. Kirchoff established that, when heated, the ability of a given substance to emit radiation is proportional to its ability of absorbing radiation. The fraction of the radiant energy which is absorbed is called absorptivity. Since the absorptivity is less than unity for all surfaces except a black body, it is clear that no surface can emit strongly than a black body. The closest realisation of black body behaviour is a well insulated heated cavity from which purely thermal radiation escapes through a small hole in one wall. An electrically heated furnance with a small opening serves as a convenient black body.

The energy of radiation emitted by hot bodies can be analysed by passage through a fluorite prism. A thermal spectrum similar to visible spectrum is obtained. For measuring the intensity of radiation corresponding to different wavelengths, a thermopile is moved along the different parts of the spectrum. The deflection of the galvanometer connected to the thermopile is proportional to the intensity of radiation.

Typical experimental results given in Fig. 1.4 lead to following conclusions.

1) The radiant energy E_λ varies with the wavelength and has a maximum value at a certain wavelength λ_{max}.

2) λ_{max} is inversely proportional to the absolute temperature of the radiator, i.e.

$$\lambda_{max} T = 0.287 \text{ cm } ^\circ\text{C} \tag{1.22}$$

A working theory was needed to explain these experimental results. Both thermodynamics and classical mechanics were used

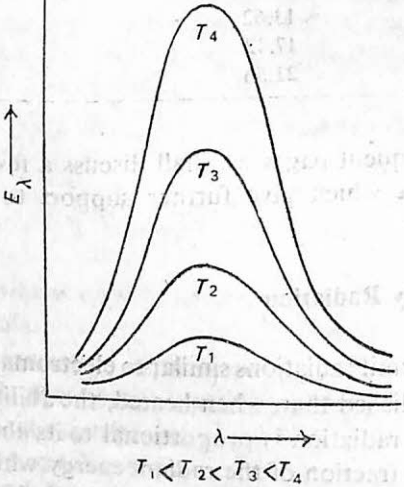


Fig. 1.4. Energy spectrum of a black body at various temperatures.

to develop a theory prior to 1900. Wien in 1896 deduced the following expression on the basis of thermodynamic agruments

$$E_\lambda = \frac{c_1}{\lambda^5}\, e^{-c_2/\lambda T} \tag{1.23}$$

where c_1 and c_2 are constants. E_λ corresponds to the position of spectrum lying between λ and $\lambda + d\lambda$. Equation (1.23) predicts a maximum as shown below. Differentiating equation (1.23), we get

$$\frac{dE}{d\lambda} = \frac{c_1}{\lambda^6}\cdot(-5)\cdot e^{-c_2/\lambda T} + \frac{c_1}{\lambda^5}\cdot e^{-c_2/\lambda T}\left(\frac{c}{T}\cdot\frac{1}{\lambda^2}\right)$$

or

$$\frac{dE}{d\lambda} = \frac{c_1}{\lambda^6}\left(\frac{c}{T\lambda} - 5\right) e^{-c_2/\lambda T} \tag{1.24}$$

We know that $dE_\lambda/d\lambda = 0$ when $\lambda = \lambda_{\max}$

Thus,

$$\frac{c_2}{\lambda_{\max}\cdot T} = 5 \tag{1.25}$$

or

$$T\cdot\lambda_{\max} = c_2/5 \tag{1.26}$$

Although Wien's equations accounts for the observed maximum in Fig. 1.4, it cannot explain the dependence of E_λ on wavelength at high temperatures and low frequencies.

Rayleigh used the following arguments to obtain an equation for E_λ based on classical mechanics. Since matter and radiation are in equilibrium under these conditions the energy dE of radiation at a particular frequency ν is equal to the number of black body oscillators of frequency between ν and $\nu + d\nu$ multiplied by the average energy $\bar{\epsilon}$ of the oscillators, so that

$$dE = dN\,\bar{\epsilon} \tag{1.27}$$

According to a general theorem of elasticity, the number of oscillators per unit volume is given by,

$$N = \frac{8\pi\,\nu^3}{3c^3} = \frac{8\pi}{3\lambda^3}$$

Hence,

$$\frac{dN}{d\nu} = \frac{8\pi\,\nu^2}{c^3};\ \frac{dN}{d\lambda} = -\frac{8\pi}{\lambda^4}$$

and

$$dE = \frac{8\pi\, \nu^2\, \bar{\epsilon}\; d\nu}{c^3} = -\,\frac{8\pi\; \bar{\epsilon}\; d\lambda}{\lambda^4} \tag{1.28}$$

Therefore the energy per unit of frequency E_ν is given by

$$E_\nu = \frac{dE}{d\nu} = \frac{8\pi\, \nu^2\; \bar{\epsilon}}{c^3} \tag{1.29}$$

and energy per wavelength unit E_λ is given by

$$E_\lambda = -\,\frac{dE}{d\lambda} = \frac{8\pi\; \bar{\epsilon}}{\lambda^4} \tag{1.30}$$

According to classical theory of equipartition of energy, $\bar{\epsilon} = kT$ so that on substitution in equation (1.29) and (1.30) we obtain,

$$E\nu = \frac{8\pi\, \nu^2\, kT}{c^3};\;\; E_\lambda = \frac{8\pi\, kT}{\lambda^4} \tag{1.31}$$

According to equation (1.31), E_λ should rapidly decrease with λ. This can be true only for the long wavelength region (see Fig. 1.6). The experimental results for the short wavelength region cannot be accounted for by equation (1.31). Thus the theory could not explain the results for the entire region of the thermal spectrum. And hence we conclude that the two theories alone cannot explain the black body thermal spectra.

In the year 1900 Planck showed that the correct form of the temperature radiation law, could be obtained on the basis of quantum hypothesis proposed by Planck. He accepted the equation $E_\lambda = \frac{8\pi}{\lambda^4}\, \bar{\epsilon}$ given by classical electrodynamics but dispensed with the expression $\bar{\epsilon}\, kT$ from the kinetic theory for the average energy of the oscillator. Instead he used equation (1.8)

Combining equation (1.30) and (1.8) he obtained,

$$E_\lambda = \frac{2\pi\, h\, c^2}{\lambda^5\, (e^{ch/k\lambda T} - 1)}$$

$$= \frac{2\pi . hc^2}{\lambda^5\, (e^{h\nu/kT} - 1)} \tag{1.32}$$

Equation (1.32) is found to be in agreement with the black body spectral results which give a strong support to the quantum hypothesis.

Another set of phenomena which could satisfactorily be explained by quantum hypothesis are the photoelectric and Compton effects.

1.3 Photoelectric Effect

When the negatively charged surface of a metal like Zinc or sodium is illuminated by light of short wavelength electrons are emitted. The effect is called a photoelectric effect.

A schematic diagram of the working of a photo cell is given in Fig. 1.5

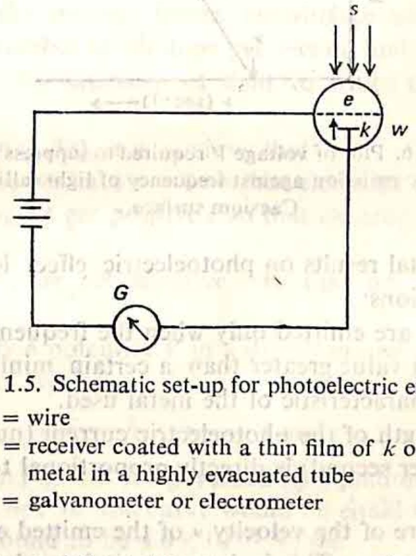


Fig. 1.5. Schematic set-up for photoelectric effect.

w = wire
k = receiver coated with a thin film of k or other metal in a highly evacuated tube
G = galvanometer or electrometer

The high vacuum of the tube serves as a complete insulator between w and k but when the receiver is exposed to light from the source s, electrons are ejected from the receiver and attracted to the positively charged wire, thus completing the circuit. The current registered by the galvanometer is directly proportional to the number, of electrons ejected per second, and this, in turn is proportional to the number of photons striking the receiver, i.e. to the intensity of the light.

An external potential V can be applied to arrest the flow of the electrons. Under these conditions,

$$\tfrac{1}{2} m v^2 = e V$$

or

$$v = (2\,Ve/m)^{1/2}$$

The voltage V required to suppress the photoelectric current increases with frequency ν of the radiation. Typical results for a metal surface are plotted in Fig. 1.6

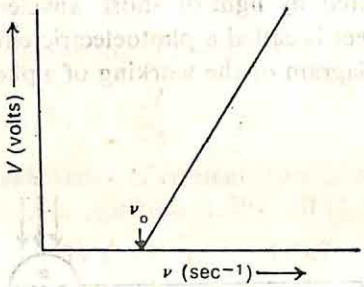


Fig. 1.6. Plot of voltage V required to suppress photo electric emission against frequency of light falling on Caesium surface.

The experimental results on photoelectric effect lead to the following conclusions:

1) Electrons are emitted only when the frequency of the incident light has a value greater than a certain minimum value ν_0. This value is characteristic of the metal used.

2) The strength of the photoelectric current (number of electrons emitted per second) is directly proportional to the intensity of light.

3) The square of the velocity ν of the emitted electrons varies with the frequency ν. This is, however, independent of the intensity of the incident light.

These experimental results do not agree with the classical electromagnetic theory of radiation according to which the velocity of the emitted electrons should depend on the light intensity and not on its frequency.

The above experimental observations can be explained on the basis of quantum hypothesis as follows.

When a photon (frequency ν) strikes the metal, a part of energy is taken up by the electron to escape from the metal surface. The balance of energy appears as kinetic energy ($mv^2/2$) of the electron so that,

$$\epsilon = h\nu = W + \frac{mv^2}{2}$$

$$= h\nu_0 + \frac{mv^2}{2} \qquad (1.33)$$

where ν_0 is the threshold frequency and W, the work function of the metal, is a measure of energy of escape of the electron from the metal surface.

From equation (1.33) we have

$$v^2 = \frac{2\,h\nu}{m} - \frac{2\,h\nu_0}{m} \qquad (1.34)$$

which shows that V^2 is directly proportional to ν. Thus the velocity with which the electron leaves the surface would be independent of the number of photons per second and would also be independent of the intensity of light to which the surface is exposed.

From equation (1.33), it is obvious that

a) when $\nu = \nu_0$ we have $v = 0$ so that electrons do not move.

b) when $\nu > \nu_0$ we get positive v so that electrons would begin to move.

c) when $\nu < \nu_0$ we get negative v so that no electrons are emitted.

When we apply a potential V in a direction opposite to movements of electrons, we have

$$e\,V = h\nu - h\nu_0 = \tfrac{1}{2}\,mv^2 \qquad (1.35)$$

Results plotted in Fig. 1.8 are governed by equation (1.35). It is clear that the slope of the curve would be equal to h/e. From Fig. 1.8, this is found to be 4.0×10^{-15} V. sec.

From this we get Planck's constant to be equal to 4.0×10^{-15} eV sec or 6.57×10^{-27} erg sec.

1.4 Compton Effect

Compton (1923) observed that when X-rays fall on a crystal, they are scattered. The experimental results show that,

1) The scattered X-rays have a lower frequency ν' than that of incident rays ν.

2) The frequency difference $(\nu - \nu')$ increases with scattering angle α which is defined in Fig. 1.7

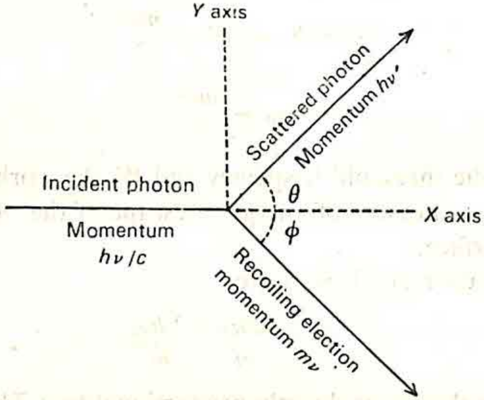


Fig. 1.7. Scattering of X photons by electrons.

The energy and momentum of photon and electron before and after collision are summarised in Table 1.5.

Table 1.5. Energy and momentum of the photon and electron during collision

		X photon	Electron
Before collision	energy	$h\nu$	0
	momentum along X-axis	$h\nu/c$	0
	momentum along Y-axis	0	0
After collision	energy	$h\nu'$	$\frac{1}{2} mv^2$
	momentum along X-axis	$\frac{h\nu'}{c} \cos\theta$	$m\,v \cos\phi$
	momentum along Y-axis	$\frac{h\nu'}{c} \sin\theta$	$m\,v \sin\phi$

The phenomena can be explained on the basis that the photons have mass and the momentum is conserved on collision with electrons.

We have from Einstein's equation $E = mc^2$ and from Planck's hypothesis we have, $E = h\nu$. Combining these results we get

$$mc = \frac{h}{\lambda} \tag{1.36}$$

Since energy is conserved

$$h\nu = h\nu' + \tfrac{1}{2}\, mv^2$$

Further since momentum is also conserved we have along X-axis (see Fig. 1.7)

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos\theta + mv \cos\phi \tag{1.37}$$

Similarily, along Y-axis we have

$$\frac{h\nu'}{c} \sin\theta = mv \sin\phi \tag{1.38}$$

Using the condition $\sin^2\phi + \cos^2\phi = 1$ and on eliminating ϕ between equations (1.37) and (1.38), we get

$$mv = \frac{2\,h\nu}{c} \cdot \frac{\sin\theta}{2}$$

and

$$\Delta\nu = \nu - \nu' = \frac{h\nu^2}{mc^2}\,(1 - \cos\theta) \tag{1.39}$$

By measuring the frequency of scattered X-radiation at different scattering angles θ, the value of Planck's constant h can be obtained from the scattering data. This value is in excellent agreement with values previously obtained from the photoelectric effect and black body radiation.

Thus we have examined following independent phenomena:

i) specific heats of solids,
ii) hydrogen spectra and critical potentials,
iii) thermal spectrum of a black body,
iv) photoelectric effect, and
v) Compton effect.

In each case, we find that the results cannot be explained on the basis of classical mechanics or thermodynamics using the concept of continuous character of energy. On the other hand theories based on quantum hypothesis are in very good agreement with experimental data confirming the foundations of quantum hypothesis.

CHAPTER 2

Dual Character of Electron and Uncertainty Principle

In Chapter 1 we have seen how the basis of quantum hypothesis was developed. Based on this concept of quantisation of energy, Bohr's theory gives a qualitative explanation of the lines in the hydrogen spectrum and predicts the frequencies of the lines correctly. It gave a picture of atom which was accepted for quite sometime. The theory assumes that electron is a particle and it moves in a definite orbit with a definite velocity. We shall see below that the position and velocity of electrons cannot be defined simultaneously with precision and thus the idea of orbiting electron is not correct. In reality electron possesses both the properties of wave as well as that of a particle. This is called dual character.

2.1 Dual Nature of Electron

In 1924 de Broglie suggested that particles might also have wave properties. Electrons of mass m and velocity v have a wavelength λ which is given by,

$$\lambda = \frac{h}{mv} \tag{2.1}$$

which is obtained by combining quantum hypothesis i.e. $E = h\nu$ with the Einstein's equation $E = mc^2$.

By substitution of appropriate values in equation (2.1) we can calculate the wavelength of the objects with a mass of 1 gm or greater. The magnitude of the wavelength is found to be very small. Equation (2.1) is the fundamental equation of de Broglie's theory. It gives the wavelength of the hypothetical matter waves associated with material particles. If an electron is being accelerated by a field of V volts, its wavelength is given by

$$\lambda = \frac{h}{\sqrt{2m\,Ve}} \cdot 300 = \frac{150}{V} \times 10^{-8} \text{ cm}$$

Wavelengths of various objects moving with different speeds can be calculated using de Broglie's equation. Some of the results are given in Table 2.1.

Table 2.1. Wavelengths of various objects

Particle	Mass (kg)	Speed ($m \cdot s^{-1}$)	Wavelength m
1-V electron	9.1×10^{-31}	5.9×10^{5}	1.2×10^{-3}
10000-V electron	9.1×10^{-31}	5.9×10^{7}	1.2×10^{-5}
Rifle bullet	1.9×10^{-3}	3.2×10^{2}	1.1×10^{-27}
Golf ball	4.5×10^{-2}	3×10	4.9×10^{-28}
Snail	1.0×10^{-2}	1×10^{-3}	6.6×10^{-23}

The wave nature of electrons was proved by an ingeneous experiment. G.P. Thomson passed an electron beam using an accelerating potential of 2,0000 to 5,0000 volts, through a very thin film of about 10^{-6} cm thickness of metal and then allowed it to fall on a photographic plate. As shown in Fig. 2.1 series of concentric rings round a central spot were formed on a plate. This showed that electron beams are diffracted similar to light beams.

2.2 Heisenberg's Uncertainty Principle

The uncertainty principle states that the simultaneous precise determination of position and momentum is not possible. Mathematically, according to this principle,

$$\begin{aligned} \Delta p_x \cdot \Delta x &\geqslant ah \\ \Delta p_y \cdot \Delta y &\geqslant ah \qquad (2.2) \\ \Delta p_z \cdot \Delta z &\geqslant ah \end{aligned}$$

LIBRARY
Date 8.7.03
Acc. No. 10696

Library

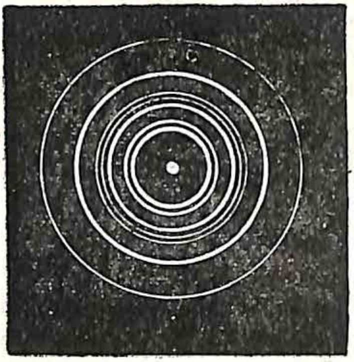


Fig. 2.1. Diffraction pattern obtained on transmission through a polycrystalline gold film.

where Δp_x is the uncertainty in momentum along X-axis, Δx is the uncertainty in position along X-axis and h is the Planck constant Δp_y and Δp_z are defined in a similar way. In the above relation a is a numerical factor of the order unity. Frequently, it is put equal to $\frac{1}{2}$. For the following discussion we shall assume that a is unity in order to simplify matters.

We would now try to explain what we mean by uncertainty. If we are measuring the distance from a fixed point A with a scale whose least count is ± 0.1 cm, then the uncertainty in our measurement would be ± 0.2 cm. In other words if we say that the distance is just 10 ± 0.2 cm., it would mean that the distance is either 9.8 cm or 10.2 cm.

Equation (2.2) can be transformed as follows:

$$\Delta v \cdot \Delta x \sim \frac{h}{m} \tag{2.3}$$

Thus if $m = 10^{-3}$ gm,

$$\Delta v \cdot \Delta x \sim 10^{-24}\ \text{cm}^2\ \text{sec}^{-1} \tag{2.4}$$

Now if Δx is known exactly say $\Delta x = 10^{-1}$ cm., uncertainty in velocity Δv would be of the order of 10^{-23} cm/sec which is too small to measure. Thus for a particle of mass of the order of $m = 10^{-3}$ gm both the position and velocity can be specified precisely. However, when $m = 10^{-27}$ gm. Heisenberg's uncertainty principle would yield.

$$\Delta x \cdot \Delta v = 1 \text{ cm}^2 \text{ sec}^{-1} \tag{2.5}$$

which indicates that if there is an uncertainty of ± 1 cm in the position of the particle, there would be an uncertainty of ± 1 cm/sec in the velocity and vice versa. Thus, for very small particles like electrons both the position and velocity cannot be ascertained precisely (See Table 1.3). Using the uncertainty principle, values of Δv have been calculated for definite values of m and for definite values of uncertainty in position. These values are recorded in Table 2.2. The table shows that if we define the position of a big particle having a large mass precisely, we can define its velocity also with great precision. However, if we are dealing with a particle like electron, the uncertainty in either position or velocity can be considerable.

Table 2.2. Values of uncertainty in velocity for definite mass and uncertainty in position ($h = 6.62\times10^{-27}$ erg. sec; $a = 1$)

Mass m gm	Uncertainty in position q, cm	Uncertainty in velocity ν, cm sec^{-1}
10^5	± 1	6×10^{-32}
1.0	± 0.001	10^{-24}
10^{-13}	$\pm 10^{-7}$	10^{-7}
10^{-24}	$+ 10^{-8}$	10^5
10^{-27}	$\pm 10^{-8}$	10^8

Following points deserve attention in connection with equation (2.2):

1) Minimum uncertainty exists whenever one tries to obtain precise values of canonical conjugates, such as position and momentum of a system at the same instant of time.

2) The uncertainty principle does not hold between variables which are not canonical conjugates. Thus, momentum of a particle in the Y-direction and its position in the X-direction can be obtained with any degree of accuracy at the same instant of time.

3) Any one of the values corresponding to these variable can be obtained at any time to a given degree of accuracy but at the same time accuracy in the determination of other variables would be affected according to equation (2.2).

For illustrating uncertainty principle we describe the famous 'thought experiment' which was suggested by Heisenberg. We

[illegible]

try to imagine an experiment which would permit the measurement of the simultaneous values of the momentum and position of a particle. For this purpose, we consider the schematic set-up shown in Fig. 2.2. In order to measure the position of the particle with precision we need a microscope. In order that the particle may be visible in the microscope at least one photon must be scattered by the particle into the microscope's eye-piece. The light can then be focussed and the position of the particle can be determined. Let us consider the determination of the position of a free particle (electron) by a microscope. Let us consider the movement of the particle in the direction of x. At any instant let the particle P subtend an angle α at the lens. If Δx is the uncertainty in the position of P and λ is the wavelength of the light illuminating it, then

$$\Delta x = \frac{\lambda}{\sin \alpha} \tag{2.6}$$

according to laws of optics governing the resolving power of any instrument.

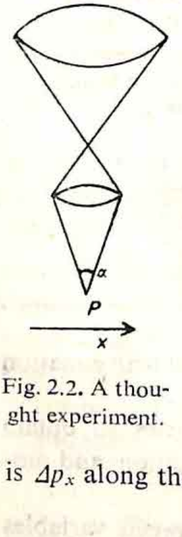


Fig. 2.2. A thought experiment.

Now, in order to observe the particle, at least one photon must be scattered from the electron so that it passes through the microscope to the eye of the observer. When the photon strikes the electron, it receives a compton recoil (see Chapter 1) of order of magnitude h/λ. The photon is scattered within the bundle of rays entering the microscope. Hence, the direction of photon cannot be determined and hence the recoil of the electron cannot be exactly known. If uncertainty of momentum is Δp_x along the x-direction

$$\Delta p_x \sim \frac{h}{\lambda} \sin \alpha \tag{2.7}$$

On combining equations (2.6) and (2.7) we get,

$$\Delta x \cdot \Delta p_x \sim h \tag{2.8}$$

Equation (2.8) can be rearranged as follows:

$$m\, \Delta v_x\, \Delta x = (m v_x\, \Delta v_x)\, \frac{\Delta x}{\Delta v_x} \tag{2.9}$$

or

$$\Delta E \cdot \Delta t \approx h \tag{2.10}$$

where $\Delta E = mv_x\,\Delta v_x$ = change in kinetic energy

and $$v_x = \frac{\Delta x}{\Delta t}.$$

Thus, Heisenberg's uncertainty principle states quantitatively the minimum uncertainties encountered when we measure quantities such as position and velocity or energy and time experimentally.

CHAPTER 3

Basis of Wave Mechanics and Schrödinger Equation

It has been pointed out in the preceding chapter that electron has wave properties and the wavelength of an electron can be calculated by de Broglie's relation. Further, according to the uncertainty principle, both the position and velocity of an electron cannot be specified simultaneously. Hence, the idea of an electron moving in an atom in a fixed orbit around the nucleus as postulated by Bohr's theory is not correct. In order to have a more realistic concept we have to consider the dual character of an electron both as a wave and particle and we have to describe its movement around the nucleus by a different type of mechanics called wave mechanics. In chapters 3 and 4, it is proposed to develop the basic methodology of wave mechanics. Before we discuss the subject in greater detail, we shall first discuss the wave equation.

3.1 Schrödinger Wave Equation

We consider a wave train moving along the X-axis with time t, ψ, λ and ν are respectively the amplitude, wavelength and the frequency of the wave as indicated in Fig. 3.1.

The wave train at $t = 0$ or any integral multiple of the period of vibration has zero amplitude. The amplitude at time t along the direction x is given by

$$\psi = A \sin 2\pi \left(\frac{x}{\lambda} - \nu t \right)$$

or
$$\psi = A \sin \frac{2\pi}{\lambda}(x - ct) \tag{3.1}$$

where
$$c = \nu\lambda$$

Differentiating equation (3.1) twice with respect to x we get
$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \cdot \psi = 0 \tag{3.2}$$

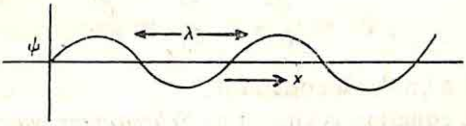


Fig. 3.1. Wave propagation along axis of x.

Equation (3.2) is the characteristic equation for all types of waves including matter waves.

Since, total energy E of the system is the sum of the kinetic energy of the electron of mass m with a velocity v and potential energy V, we have
$$E = \tfrac{1}{2}\, m v^2 + V \tag{3.3}$$

where V would depend on the position coordinates of this electron.

From de Broglie's relation which is the generalised form of equation (1.36) for matter waves, momentum $= h/\lambda$,
$$\text{i.e. } mv^2 = \frac{h^2}{m\lambda^2} \tag{3.4}$$

Using equations (3.3) and (3.4) we have,
$$2(E - V) = \frac{h^2}{m\lambda^2}$$

or
$$\frac{1}{\lambda^2} = \frac{2m(E - V)}{h^2} \tag{3.5}$$

Putting the value of $1/\lambda^2$ in equation (3.2), we get
$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{3.6}$$

This is the wave equation for the particle moving along X-axis.

But when the particle is moving in a three-dimensional space, the equation takes the following form,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

or

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{3.7}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and is called a Laplacian operator.*

The above equation is known as *Schrödinger wave equation.* It shows how ψ depends on the position co-ordinates, of the electron in a system of fixed E and V.

In polar co-ordinates (r, θ, ϕ), the Laplacian operation ∇^2 is represented by

$$\nabla^2 = \frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2} \tag{3.8}$$

The Schrödinger equation is also written in an operator form in the following manner,

$$\left(\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right)\psi = E\psi \tag{3.9}$$

or

$$H\psi = E\psi \tag{3.10}$$

where $H = \left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)$ is called the Quantum-mechanical Hamiltonian operator. ψ and E are called the eigen-function and eigen value respectively. The state of the system described by Ψ is called an eigen state.

The solution of Schrödinger equation yields the values of (i) E for the system, and (ii) $\psi_{(x)}$ or $\psi_{(x,y,z)}$ at various points and hence the probability of finding the electrons.

---

*An operator signifies a mathematical operation. Thus in $\sqrt{x}$ the symbol, square root is an operator and gives the result of operation on x. Similarly d/dx and d^2/dx^2 are operators.

When time is also a variable, E in equation (3.10) is replaced by differential operator, $-\frac{h}{2\pi_i}\cdot\frac{\partial}{\partial t}$ so that

$$H\psi = -\frac{h}{2\pi_i}\cdot\frac{\partial\psi}{\partial t} \tag{3.11}$$

Equation (3.11) is called the time-dependent Schrödinger equation.

There are three ways of introducing the wave equation at elementary level.

i) The equation may be presented without giving proof.

ii) One may start with the discussion of Physics and Mathematics of wave motion along with the discussions of the differential equation,

$$\nabla^2 u = \frac{1}{c^2}\cdot\frac{\partial^2 u}{\partial t^2}$$

and its most general solution where c is a constant having dimensions of velocity, t is the time and u is a characteristic entity. u is a mechanical displacement in the case of transverse vibration of a stretched string. In case of the particle wave $u = \psi$. However, it is difficult to give any physical interpretation of the quantity ψ for electron waves except that ψ^2 is a measure of electron density.

iii) A postulatory approach may be used for introducing the basic idea of quantum mechanics as outlined by Kauzman and Hanna. The Schrödinger equation follows logically on the basis of these postulates.

While the last approach is mathematically rigorous and logically reasonable as compared to the second one, it is a little difficult for the beginners to appreciate or comprehend the postulatory approach. The development of rigorous approach is certainly desirable at an advanced level.

3.2 Significance of ψ-function

ψ^2 is called the probability distribution function only if ψ is a single-valued function. In general the square of modulus of ψ is the probability density whereas $\psi^2\, d\tau$ is the probability of finding the particle in the volume element $d\tau$ which is equal to $dx\ dy\ dz$ in the cartesian co-ordinates. The probability density is expressed as $\psi\,\psi^*$ where ψ^* is the complex conjugate of ψ. $\psi\,\psi^*$ is always real and non-negative, thus justifying its relation to probability. This can be understood in the following manner. Let $z = x + iy$ where z is a complex number and x and y are real numbers. Then $z^* = x - iy$ and $zz^* = x^2 + y^2$ is a real non-negative number.

In order to have a physical concept of ψ and ψ^2 we may imagine as follows. Let us consider a system containing a nucleus and an electron. Let us suppose that at a particular moment we were able to determine exactly where the electron existed. Let us represent the position by a dot in space of three-dimension. We put similar dots for various positions of electrons as the electron moves in space. After a certain period, we shall obtain a distribution of dots as shown in Fig. 3.2.

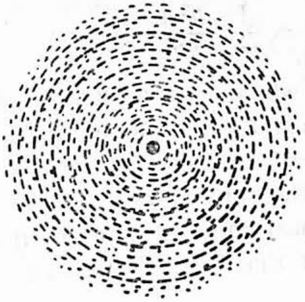


Fig. 3.2. Electron cloud.

Figure 3.2 gives the impression of an electron cloud around the nucleus. The cloud would be dense in the regions where the number of dots are more i.e. where the probability of finding the electron is more. Thus the density of the charge cloud is a measure of probability $\psi^2\,d\tau$ of finding the electron in the volume element $d\tau$. The probability density is defined as follows

$$\begin{aligned}\text{Probability density} &= \frac{\text{Probability}}{\text{Volume}}\\ &= \frac{\psi^2\,d\tau}{d\tau}\\ &= \psi^2 \qquad (3.12)\end{aligned}$$

In view of the above relationship between ψ^2 and probability density, ψ-function must satisfy the following conditions:

i) it must be single-valued,

ii) it must be finite and continuous, and

iii) The first space and time derivative of the ψ-function must also be continuous.

These limitations can be easily conceived since probability must be finite and it cannot have two values at the same point.

In addition to the above, there are other important properties of the wave functions which are discussed below:

1) Since the total probability over all available space must be unity.

$$\int |\psi|^2 d\tau = \int \psi\,\psi^* d\tau = 1 \tag{3.13}$$

Equation (3.13) is known as the normalisation condition.

2) If an electron can exist in two different quantum states corresponding to the wave function $\psi_a^{(1)}$ and $\psi_b^{(2)}$, it can be shown that

$$\int \psi_a^{(1)}\ \psi_b^{(2)}\ d\tau = 0 \tag{3.14}$$

This equation is called the orthogonality theorem, which can be derived in the following way:

The wave equation for the two quantum states *a* and *b* can be written as follows,

$$\nabla^2 \psi_a + \frac{8\pi^2 m}{h^2}(E_a - V)\,\psi_a = 0 \tag{3.15}$$

$$\nabla^2 \psi_b + \frac{8\pi^2 m}{h^2}(E_b - V)\,\psi_b = 0 \tag{3.16}$$

where we have dropped the superscripts (1) and (2).

Multiplying Eq. (3.15) by ψ_b and (3.16) by ψ_a integrating over the whole space and then taking the difference, we get

$$\int \Big(\psi_b \nabla^2 \psi_a - \psi_a \nabla^2 \psi_b)\,d\tau = -\frac{8\pi^2 m}{h^2}(E_a - E_b)\int \phi_a \psi_b\,d\tau \tag{3.17}$$

In the first instance we consider the integration over x from $-\infty$ to ∞. Integrating the left hand side by parts we have

$$\int_{-\infty}^{+\infty} \left(\psi_b \frac{\partial^2}{\partial x^2}\psi_a - \psi_a \frac{\partial^2}{\partial x^2}\psi_b\right) dx = \Big|\Big(\psi_b \frac{\partial}{\partial x}\psi_a$$

$$-\psi_a \frac{\partial}{\partial x}\,\psi_b\Big)\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\left(\frac{\partial\psi_b}{\partial x}\cdot\frac{\partial\psi_a}{\partial x} - \frac{\partial\psi_a}{\partial x}\cdot\frac{\partial\psi_b}{\partial x}\right) dx \tag{3.18}$$

The integral on the right is obviously zero. The first term on the right hand side has to be evaluated for infinite distance within limit from $-\infty$ to $+\infty$, but here the wave-function must vanish. This is indeed the boundary condition which we have to impose on all wave functions. The integral of left hand side of equation (3.18) therefore vanishes when the L.H.S. of equation (3.17) is integrated over x from $+\infty$ to $-\infty$.

Hence the left hand side of equation (3.17) vanishes and we, always have

$$(E_a - E_b)\int \psi_a\cdot\psi_b\cdot d\tau = 0 \tag{3.19}$$

If now a and b are states with two different energies the integral of equation (3.19) must vanish, which proves equation (3.14). The above relation need not necessarily hold when ψ_a and ψ_b are two different wave-functions belonging to the same energy.

3) The average energy $\bar{E}$ is related to wave-function in the following manner,

$$\bar{E} = \frac{\int \psi^* H\psi\, d\tau}{\int \psi^*\, \psi\, d\tau} \tag{3.20}$$

where H is Hamiltonian operator.

3.3 Solution of the Wave Equation

Solution of Schrödinger equation can be easily guessed since it is a linear differential equation. Thus,

a) If ψ is a solution of the wave equation, $c\psi$ would also be a solution where c is an arbitrary constant.

b) If ψ_1 and ψ_2 are the two solutions of the wave equation then $c_1\psi_1 \pm c_2\psi_2$ would also be a solution of the wave-equation where C_1 and C_2 are constants. Case (b) is utilized in constructing hybrid orbitals by combining wave-functions.

If there are two wave function $\psi_a^{(1)}$ and $\psi_b^{(2)}$ for two electrons

1 and 2 in a molecule having similar energies, then we can get molecular wave-function $\bar{\psi}$ as follows,

$$\bar{\psi} = a_1\psi_a^{(1)} \pm a_2\psi_b^{(2)} \tag{3.21}$$

where a_1 and a_2 are constants. Equation (3.21) has been utilised in constructing molecular orbitals from atomic orbitals. The procedure is called linear combination of atomic orbitals which is abbreviated as L.C.A.O. For constructing molecular orbitals, following requirements have to be satisfied (i) $\psi_a^{(1)}$ and $\psi_b^{(2)}$ must be orbitals of similar energies. (ii) The A.O.'s must have the same symmetry with respect to intermolecular axis.

We can also have another solution $\bar{\psi}_2$ such that

$$\bar{\psi}_2 = \psi_a^{(1)}\ \psi_b^{(2)} \tag{3.22}$$

based on the fact that the composite probability would be product of individual probabilities. $\bar{\psi}_2$ would be a solution of the wave equation for two electrons with no interaction between them.

If ϕ_1 and ϕ_2 are the normalised wave functions of the two electrons 1 and 2 then molecular orbitals can be written as follows

$$\psi^+ = c_1\,\phi_1 + c_2\,\phi_2 \tag{3.23}$$

$$\psi^- = c_1\,\phi_1 - c_2\,\phi_2 \tag{3.24}$$

The values of the coefficients c_1 and c_2 can be determined by

---

We can use postulatory approach straightway to develop wave machanics. The basic postulates can be stated as follows:

I) The physical state of a particle at time t is described by a complex wave function $\psi\ (x, t)$.

II) The wave function $\Psi\ (x, t)$ and its first and second derivatives $\frac{\partial\psi\ (x, t)}{\partial x}$, $\frac{\partial^2\psi\ (x, t)}{\partial x^2}$ must be continuous, finite and single valued for all values of x in view of relationship of the wave function with the probability amplitude.

III) The average or expectation value $\langle F \rangle$ of any observable F, which corresponds to an operator $\hat{F}$ is calculated from the formula

$$< F > = \int_{-\infty}^{\infty} \psi^*\ \hat{F}\,\psi\ dx$$

It is assumed that the wave function is normalised.

using (i) normalisation condition, and (ii) orthogonality theorem. This is done below.

Applying the normalisation condition for ψ^*, we have

$$\int \psi^+ \psi^{+*} \, d\tau = \int (c_1 \phi_1 + c_2 \phi_2)(c_1 \phi_1^* + c_2 \phi_2^*) \, d\tau$$

$$= \int (c_1 \phi_1 \, c_1 \phi_1^*) \, d\tau + \int (c_2 \phi_2 \, c_2 \phi_2^*) \, d\tau$$

$$+ \int (c_1 \phi_1^* \cdot c_2 \phi_2) \, d\tau + \int c_2 \phi_2^* \, c_1 \, \phi_1 \, d\tau \qquad (3.25)$$

Using the normalisation condition and the orthogonality theorem we get,

$$\int \psi_+ \psi_+^* \, d\tau = c_1^2 + c_2^2 + 0 + 0 = 1 \qquad (3.25)$$

Hence

$$|c_1|^2 + |c_2|^2 = 1 \qquad (3.26)$$

The orthogonality theorem yields,

$$\int \psi_+^* \, \psi_- \, d\tau = \int (c_1 \phi_1 + c_2 \phi_2)^* (c_1 \phi_1 - c_2 \phi_2) \, d\tau = 0 \qquad (3.27)$$

On solving we have,

$$c_1^2 - c_2^2 = 0 \qquad (3.28)$$

From equations (3.26) and (3.28) it follows that

$$c_1 = c_2 = \pm \frac{1}{\sqrt{2}} \qquad (3.29)$$

3.4 Approximate Solutions of Schrödinger Equation

Accurate solution of Schrödinger equation has only been obtained for a one-electron system as we shall see in the next chapter. The chemical species of interest are many electron system for which Schrödinger equation defies an exact solution. Hence approximation methods have been developed which are discussed below:

1) VARIATION METHOD

From the chemist's viewpoint, the evaluation of E is more important. Equation (3.20) can be used for this purpose, but the major difficulty is in choosing the appropriate ψ function. However, one can use any trial function, the calculated energy $E \geqslant E_0$ where E_0 is the true value. We may note that E_0 is the minimum obtainable value. For any trial function used we may obtain a minimum value, E_{min} by adjusting the constant in the wave function. The values of E_{min} would naturally depend on the choice of the trial function ψ. For any choice of ψ, $E_{min} \geqslant E_0$ and $E_{min} = E_0$ only if the trial function ψ is identical with the true wave function for the system. Let us suppose that $\psi = \sum_{k=1} c_k \phi_k$ where ϕ_k are the atomic orbitals and c_k are the coefficients. The condition for minima i.e. $\frac{\partial E}{\partial c_k} = 0 \ldots (k = 1, \ldots k)$ would yield relations which can be used for choosing the wave function which would give a minimum value of E. These conditions give a set of equations on solving which E is obtained. The method is illustrated in Chapters 5, 7 and 10.

2) PERTURBATION METHOD

When there is no perturbation, the wave function of an atom would be represented by

$$H^\circ \psi = E^\circ \psi \tag{3.30}$$

where H° is the unperturbed Hamiltonian and E° is the corresponding unperturbed eigenvalue. In an electric or magnetic field, the Hamiltonian would be perturbed and effective Hamiltonian H would be given by

$$H = H^\circ + H' \tag{3.31}$$

where H' is the perturbation in the Hamiltonian operator. The corresponding eigenvalues would then be given by

$$E = E^\circ + E' \tag{3.32}$$

These can be evaluated by using equation (3.20) i.e.

$$E = \frac{\int \psi^{\circ *} H \psi^\circ \, d\tau}{\int \psi^* \psi \, d\tau}$$

where ψ° is the wave function of the unperturbed state. Substituting H from equation (3.31)

$$E = \frac{\int \psi^{\circ *} (H^{\circ} + H') \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$= \frac{\int \psi^* H^{\circ} \psi \, d\tau}{\int \psi^* \psi \, d\tau} + \frac{\int \psi^* H' \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad (3.33)$$

In above equation first term would be equal to the energy of unperturbed state, E_0 and the second term would be equal to the energy of the perturbed state E'. So that

$$E' = \frac{\int \psi^* H' \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad (3.34)$$

Energy for He atom has been evaluated by first considering the one-electron system with the nuclear charge + 2 and then taking into account the perturbation by the second electron. The method is useful for the study of London dispersion forces and charge transfer forces. The third order and fourth order perturbation theory has been used for estimating the first hyperpolarisability and second hyperpolarisability of the molecules. The approach is useful for the interpretation of Stark and Zeeman effects.

CHAPTER 4

Wave Mechanics of Free Electrons

4.1 Free Particle in a Box

Quantum hypothesis discussed in Chapter 1 and the Schrödinger wave equation described in Chapter 3 may appear in the first instance to be unrelated. In this chapter we consider a system in which electron is free to move within rigid boundaries. We shall see that the solution of the Schrödinger equation for the case yields certain permissible values of energies similar to that prescribed by the quantum hypothesis. Further we shall see for this case that the wave function must be finite, continuous and single-valued.

We consider a particle confined to move within a rectangular box as shown in Fig. 4.1 We take 0 as the origin and the three mutually perpendicular edges as x, y and z axes. Such a restriction means that beyond the sides of the box potential energy $V = \infty$ whereas inside the box $V = 0$. The potential energy diagram is shown in Fig. 4.2. Let us represent the wave function of the particle moving along the axis x by $\psi(x)$, then the Schrödinger wave equation can be written as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{4.1}$$

Since $V = 0$, equation (4.1) reduce to

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

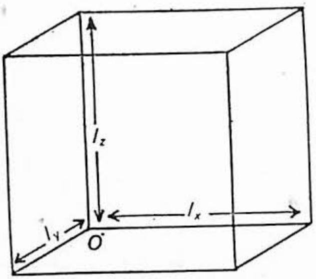


Fig. 4.1. Rectangular box.

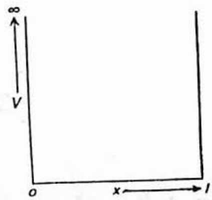


Fig. 4.2. Linear potential box.

which can be written as,

$$\frac{\partial^2 \psi}{\partial x^2} + x^2 \psi = 0 \tag{4.2}$$

where

$$x^2 = \frac{8\pi^2 m E}{h^2} \tag{4.3}$$

The solution of equation (4.2) would be of the form

$$\psi_{(x)} = C\, e^{+ikx} + D\, e^{-ikx}$$

where C and D are constants.

Since the electron cannot be found beyond $x = 0$ and $x = 1$, we must have $\psi_{(0)} = 0$ and $\psi_{(l)} = 0$.

Therefore,

$$C + D = 0 \tag{4.5}$$

and

$$C\, e^{ikl} + D\, e^{-ikl} = 0 \tag{4.6}$$

Combining equations (4.5) and (4.6) we get

$$e^{ikl} - e^{-ikl} = 0 \tag{4.7}$$

Since

$$\sin kl = \frac{e^{ikl} - e^{-ikl}}{2i}$$

Therefore, on account of equation (4.7), $\sin kl = 0$

Hence,

$$k = \frac{n_x \pi}{l} \tag{4.8}$$

So that

$$\psi(x) = A \sin \frac{n_x \pi x}{l} \tag{4.9}$$

where $A = 2iC$

and $n_x = 1, 2, 3, \ldots$

The solution shows that mathematically the problem under consideration is identical with that of vibrating spring fixed at both ends. We can determine the value of A as follows. When ψ is normalised,

$$\int_0^l \psi^2_{(x)}\, dx = 1$$

or

$$\int_0^l A^2 \left\{\sin\left(\frac{n_x \pi x}{l}\right)\right\}^2 dx = 1$$

or

$$\int_0^l \left\{1 - \cos\left(\frac{2n_x \pi x}{l}\right)\right\} dx = \frac{2}{A^2}$$

or

$$A^2 = \frac{2}{l}$$

$\therefore$

$$A = \left(\frac{2}{l}\right)^{1/2} \tag{4.10}$$

Thus, the complete solution of equation (4.1) yields

$$\psi_{(x)} = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{n_x \pi x}{l}\right) \tag{4.11}$$

We shall now discuss a few results which follow from the above treatment. Combining equations (4.3) and (4.8) we get

$$E_n = \frac{n_x^2 h^2}{8m\, l^2} \tag{4.12}$$

which shows that the energy of the particle can have only definite sets of values, thereby confirming that energy is quantised.

Equation (4.12) can also be obtained by using equations (4.9) and (3.20).

Using equation (4.11) for plotting $\psi(x)$ as a function of x for $n_x = 1$, $n_x = 2$, $n_x = 3$, we get the set of curves shown in Fig. 4.3. It is obvious that there are regions inside the box where the probability of finding the electron can be zero. Such regions are called nodes while antinodes are the regions where the probability is maximum. We can conveniently demonstrate the existence of nodes by plotting $|\psi_{(x)}|^2$ as a function of x noting that

$$\text{Probability density } |\psi_{(x)}|^2 = \left(\frac{2}{l}\right) \sin^2\left(\frac{n_x \pi x}{l}\right) \quad (4.13)$$

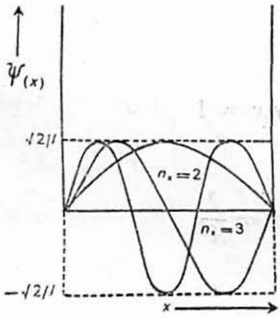


Fig. 4.3. Wave function $\psi(x)$ for free particle in a box for various values of n.

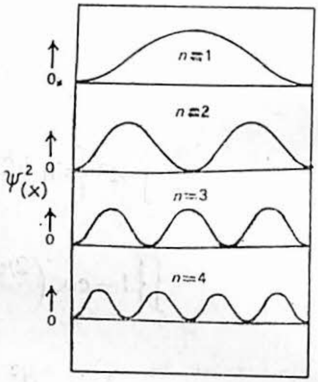


Fig. 4.4. $\psi^2(x)$ as a function of x for different values of n_x.

From Fig. 4.4, it is obvious that as n increases, the number of nodes and antinodes for $\psi^2(x)$ also increase.

4.2 Particle in a Rectangular Three-dimensional Box

For a particle in a three-dimensional box of length l_x, l_y, l_z the wave function will be a function of all the three space-coordinates. Further,

$$V = 0 \quad \text{for} \quad 0 < x < l_x;\ 0 < y < l_y;\ 0 < z < l_z$$

where l_x, l_y, l_z are the sides of the walls.

The Schrödinger equation for the particle inside the box is given by

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}E\psi=0 \tag{4.14}$$

Since ψ is a function of x, y, z and since the solution of the above equation has to be valid for (i) $x = 0$, $y = 0$, (ii) $y = 0$, $z = 0$, and (iii) $x = 0$, $z = 0$, it is appropriate to put where f_x, f_y, f_z are sine or exponential functions. In the above f_x is a function of x alone, f_y is a function of y alone and f_z is a function of z alone.

Therefore,

$$\frac{\partial^2\psi}{\partial x^2}=f_y\cdot f_z\cdot\frac{\partial^2 f_x}{\partial x^2} \tag{4.15}$$

$$\frac{\partial^2\psi}{\partial y^2}=f_x\cdot f_z\cdot\frac{\partial^2 f_y}{\partial y^2} \tag{4.16}$$

$$\frac{\partial^2\psi}{\partial z^2}=f_x\cdot f_y\cdot\frac{\partial^2 f_z}{\partial z^2} \tag{4.17}$$

Hence equation (4.14) can be written as

$$f_y\cdot f_z\cdot\frac{\partial^2 f_x}{\partial x^2}+f_x\cdot f_y\cdot\frac{\partial^2 f_y}{\partial y^2}+f_x\cdot f_y\cdot\frac{\partial^2 f_z}{\partial z^2}+\frac{8\pi^2 m}{h^2}E\cdot f_x\cdot f_y\cdot f_z=0 \tag{4.18}$$

Dividing throughout by

$$\frac{8\pi^2 m}{h^2}\cdot f_x\cdot f_y\cdot f_z$$

we have

$$\frac{h^2}{8\pi^2 m}\left[\frac{1}{f_x}\cdot\frac{\partial^2 f_x}{\partial x^2}+\frac{1}{f_y}\cdot\frac{\partial^2 f_y}{\partial y^2}+\frac{1}{f_z}\cdot\frac{\partial^2 f_z}{\partial z^2}\right]+E=0 \tag{4.19}$$

We put the total energy E as the sum of three energies along x, y, z axes i.e.

$$E=E_x+E_y+E_z \tag{4.20}$$

Now we can write,

$$\frac{h^2}{8\pi^2 m}\cdot\frac{1}{f_x}\cdot\frac{\partial^2 f_x}{\partial x^2}=-E_x \tag{4.21}$$

The second order differential equation (4.21) is similar to equation (4.2). Hence the solution of equation (4.21) can be written as

$$f_x = \sqrt{\frac{2}{f_x}} \cdot \sin\left(\frac{n_x \cdot \pi \cdot x}{l_x}\right) \qquad (4.22)$$

and

$$E_x = \frac{n_x^2\, h^2}{8m\, l_x^2}$$

We would obtain similar solutions for f_y and f_z so that

$$E \text{ (total energy)} = E_x + E_y + E_z \qquad (4.24)$$

i.e.

$$E = \frac{h^2}{8m} \cdot \left\{ \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right\} \qquad (4.25)$$

and

$$\psi_{(x,y,z)} = \sqrt{\frac{8}{l_x\, l_y\, l_z}} \cdot \sin\frac{n_x \cdot \pi \cdot x}{l_x} \sin\frac{n_y \cdot \pi \cdot y}{l_y} \sin\frac{n_z \cdot \pi \cdot z}{l_z} \qquad (4.26)$$

Following inferences follow from equation (4.25)

i) If the mass of the particle is smaller, the value of E is greater.

ii) Smaller the box, greater the value of E.

Equation (4.25) also shows how degeneracy arises. Number of equivalent energy states is equal to degeneracy factor. Some of the degenerate energy levels are given in Table 4.1 and illustrated in Fig. 4.5.

From Table 4.1 it is clear that the lowest value of energy $E = \dfrac{3h^2}{8ml^2}$ since minimum value of n_x, n_y, and n_z can only be equal to unity. We thus find that $3\, h^2/8\, ml^2$ is the zero-point energy.

We shall now consider the case of a free particle moving in a ring.

4.3 Particle in a Ring

Let a particle of mass m be restricted to move on the circumference of a circle of radius r, on which the potential energy is zero. The angular coordinate ϕ can vary from 0 to 360°. On transforming the coordinates of Schrödinger equation (3.7) to polar

Table 4.1. Degenerate energy levels for a particle in a box ($l_x = l_y = l_z = l$)

n_x	n_y	n_z	Energy	Remarks
1	1	1	$3h^2/8ml^2$	Single state
2	1	1	$6h^2/8ml^2$	Three degenerate state
1	2	1		
1	1	2		
2	2	1	$9h^2/8ml^2$	,, ,, ,,
2	1	2		
1	2	2		
3	1	1	$11h^2/8ml^2$	,, ,, ,,
1	3	1		
1	1	3		
2	2	2	$12h^2/8ml^2$	Single state

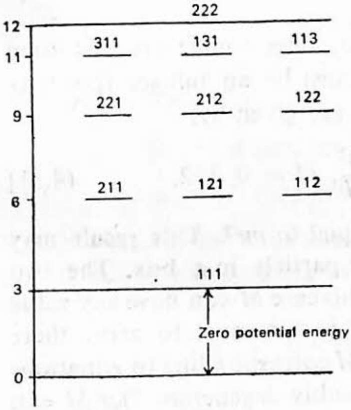


Fig. 4.5. Degenerate enery levels in a cube of length l.

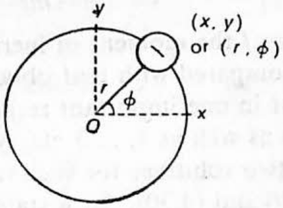


Fig. 4.6. Coordinates of a particle in a ring.

coordinates for the case, is as follows:

$$\frac{1}{r^2} \cdot \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \qquad (4.26)$$

since

$$x = r\cos\phi;\ y = r\sin\phi$$

$$r = (x^2 + y^2)^{1/2} \text{ and } \tan\phi = \frac{y}{x}$$

and

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\cdot\frac{\partial^2\psi}{\partial\phi^2} = \frac{1}{r^2}\cdot\frac{\partial^2\psi}{\partial\phi^2} \tag{4.27}$$

The potential energy around the circular path is zero so that, equation (4.26) can be written as

$$\frac{1}{r^2}\cdot\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}E\,\psi = 0 \tag{4.28}$$

One can guess immediately two solutions of equation (4.28) as follows:

$$\psi' = N_m \sin M\phi \tag{4.29}$$

$$\psi'' = N_m\cdot\cos M\phi \tag{4.30}$$

where

$$M^2 = \frac{8\pi^2 m\,r^2}{h^2}\cdot E$$

and N_m is the normalisation constant. Since ϕ must have the same value for each increment of 2π, M must be an integer (positive, negative or zero). The energy levels are given by,

$$E_M = \frac{M^2 h^2}{8\pi^2 mr^2} = \frac{M^2 h^2}{8\pi^2 I},\ M = 0, 1, 2, \tag{4.31}$$

where I the moment of inertia, is equal to mr^2. This result may be compared with that obtained for particle in a box. The two differ in one important respect. In this case M can have any value zero as well as 1, 2, 3 etc. When M is not equal to zero, there are two solutions for each value of M corresponding to equations (4.29) and (4.30). Such states are doubly degenerate. For $M = 0$ there is only one solution corresponding to equation (4.29), since $\sin 0 = 0$, and the solution of equation (4.29) yields,

$$\psi_0 = N_0, \text{ where } N_0 \text{ is constant.}$$

Further since $\int_0^{2\pi} N_0^2\,d\phi = 1$ on account of normalisation condition we will have $N_0 = 1/\sqrt{2\pi}$. Likewise N_1, N_2 etc. would be given by

$$N_m^2 \int_0^{2\pi} \sin^2 M\phi \, d\phi = \int_0^{2\pi} \frac{N_m^2}{2} (1 - \cos 2 M\phi) \, d\phi = 1 \tag{4.32}$$

so that

$$N_1 = N_2 = N_3 = \ldots . = \frac{1}{\sqrt{\pi}} \tag{4.33}$$

We can have another solution of equation (4.28) which is essentially a combination of solutions (4.29) and (4.30) so that,

$$\psi = a \cdot \frac{1}{\sqrt{\pi}} \sin M\phi + b \cdot \frac{1}{\sqrt{\pi}} \cos M\phi \tag{4.34}$$

It can be shown that a and b would be given by

$$a = \cos \alpha ; \; b = \sin \alpha$$

where α is a constant.

Equation (4.28) can also be written as

$$\psi = \frac{1}{\sqrt{\pi}} \sin (M\phi + \alpha) \tag{4.35}$$

Sometimes, it is convenient to choose the following complex orthogonal combination as the solution of the equation (4.28)

$$\psi_+ = A (\cos m\phi + i \sin m\phi) = Ae^{+im\phi} \tag{4.36}$$

$$\psi_- = A (\cos m\phi - i \sin m\phi) = Ae^{-im\phi} \tag{4.37}$$

where A and m are constants.

The above solutions are orthogonal since,

$$\int_0^{2\pi} \psi_+ \psi_- \, d\phi = \int_0^{2\pi} A^2 \, e^{-2im\phi} \, d\phi$$

$$= A^2 \int_0^{2\pi} (\cos 2 m\phi - i \sin 2 m \, \phi) \, d\phi = 0 \tag{4.38}$$

Further, since on account of normalisation condition,

$$\int_0^{2\pi} \psi_+^* \, \psi_- \, d\phi = A^2 \int_0^{2\pi} d\phi = A^2 (2\pi) = 1 \tag{4.39}$$

we have

$$A = 1/\sqrt{2\pi}$$

The case of free particle in a ring is of interest in quantum chemistry of benzene since in the case of benzene, the electron can be assumed to move in a circle of radius 0.14×10^{-7} cm.

4.4 Particle on the Surface of a Sphere

Now, for a particle restricted to move on the surface of a sphere of radius r, the Schrödinger equation in term of θ and ϕ is given by

$$\frac{1}{r^2}\cdot\frac{\partial^2\psi}{\partial\theta^2} + \frac{\cos\theta}{r^2\sin\theta}\cdot\frac{\partial\psi}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}\cdot E\psi = 0 \tag{4.40}$$

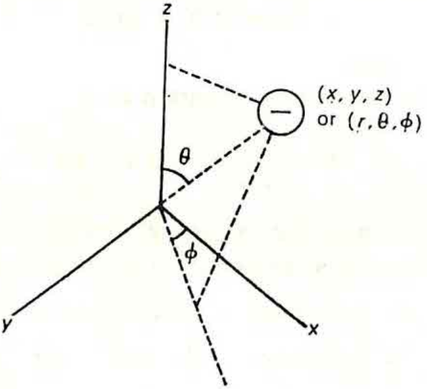


Fig. 4.7. Co-ordinates of free particle on a sphere.
$x = r\sin\theta\cos\phi$; $y = r\sin\theta\sin\phi$; $z = r\cos\theta$.

We assume that the wave function ψ can be written as follows,

$$\psi = f_2(\theta)\cdot f_3(\phi) \tag{4.41}$$

where f_2 is a function of θ alone and f_3 is a function of ϕ alone. On substitution and rearrangement we get

$$\sin^2\theta\cdot\frac{1}{f_2}\cdot\frac{\partial^2 f_2}{\partial\theta^2} + \sin\theta\cdot\cos\theta\cdot\frac{1}{f_2}\cdot\frac{\partial f_2}{\partial\theta} + \frac{8\pi^2 mr^2\sin^2\theta\cdot E}{h^2} + \frac{1}{f_3}\cdot\frac{\partial^2 f_3}{\partial\phi^2} = 0 \tag{4.42}$$

Since, the first three terms of equation (4.42) are dependent on θ only whereas f_3 depends on ϕ only, we must have

$$\frac{1}{f_3}\cdot\frac{d^2 f_3}{d\phi^2} = \text{constant} = - M^2 \tag{4.43}$$

On account of equation (4.43) we must necessarily have,

$$\frac{\partial^2 f_2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\cdot\frac{\partial f_2}{\partial\theta} - \frac{M^2}{\sin^2\theta}\cdot f_2 + \beta f_2 = 0 \tag{4.44}$$

where

$$\beta = \frac{8\pi^2 mr^2}{h^2} \tag{4.45}$$

Following is the basic difference with the three-dimensional case of a free particle in a box so far as the solution of Schrödinger equation is concerned. The solution for f_2 is dependent on M which means that it is dependent on the function f_3.

When $M = 0$ equation (4.44) becomes,

$$\frac{\partial^2 f_2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\cdot\frac{\partial f_2}{\partial\theta} + \beta f_2 = 0 \tag{4.46}$$

For getting rigorous solution of equation (4.46), we need a lengthy procedure. One of the simplest solution is f_2 = constant with $\beta = 0$. We can guess other solutions with β having different finite values. Values of β along with the form of f_2 are given in Table 4.2.

Table 4.2. Other solutions of equation (4.46)

f_2	β
a constant N_0	0
$N_1 \cos\theta$	2
$N_2\,(3\cos^3\theta - 1)$	6
$N_3\,(5/3\cos^3\theta - \cos\theta)$	12

If we put $\beta = l\,(l+1)$

we get

$$\beta = \frac{8\pi^2 mr^2\, E}{h^2} = l\,(l+1)$$

so that

$$E = \frac{h^2}{8\pi^2 mr^2}\cdot l\,(l+1) \tag{4.47}$$

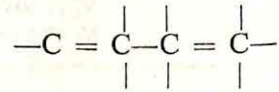
Following table gives the values of ψ-function corresponding to definite values of l and M. The functions are not normalised.

l	M	ψ	$\psi\psi^*$
0	0	constant	constant
1	0	$\cos\theta$	$\cos^2\theta$
	± 1	$\sin\theta\sin\phi$ and $\sin\theta\cos\phi$	$\sin^2\theta\sin^2\phi$ and $\sin^2\theta\cos^2\phi$
2	0	$3\cos^2\theta-1$	$(3\cos^2\theta-1)^2$
	± 1	$\sin\theta\cos\theta\sin\phi$ and $\sin\theta\cos\theta\cos\phi$	$\sin^2\theta\cos^2\theta\sin^2\phi$ and $\sin^2\theta\cos^2\theta\cos^2\phi$
	± 2	$\sin 2\theta\sin 2\phi$ and $\sin^2\theta\cos 2\phi$	$\sin^4\theta\cdot\sin^2 2\phi$ and $\sin^4\theta\cdot\cos^2 2\phi$

When $\psi\psi^*$ is plotted against θ for $l = 1$, $M = 0, \pm 1$, curves similar to the p-orbitals of hydrogen atom are obtained.

In the above paragraphs we have examined the solutions of Schrödinger equation for different cases. It has been demonstrated, how quantisation, quantum numbers, energy levels and zero point energy arise in the case of a free particle in a box or in a ring or on the surface of a sphere. We shall consider the applications of a few of the above results in chemical systems.

4.5 Applications of the Free-electron Model to Chemical Systems

The open chain polyenes of the type  $-\mathrm{C}=\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}=\overset{|}{\underset{|}{\mathrm{C}}}-$ having π-electrons approximate to the case of a free particle moving in one dimension. The electrons cannot move beyond the terminal carbon atoms, since the potential energy is infinity at the ends of the chain.

In a polyene the number of carbon atoms are $2N$ if we have N double bonds. The number of π-electrons would therefore be equal to $2N$. It is obvious that in the ground state, N levels must be filled. The excitation would occur when one or more of those electrons are excited to $(N+1)$ or higher energy levels. Accordingly the first excitation energy would be given by

$$\Delta E = [N+1)^2 - N^2]\, h^2/8ml^2 = (2N+1)\, h^2/8ml^2 \qquad (4.48)$$

Since $\Delta E = \frac{hc}{\lambda}$, we have

$$l = \sqrt{(2N+1)\, h\lambda/8mc} \qquad (4.49)$$

When l and λ are both measured in Å the above expression reduces to,

$$l = 5.507 \times 10^{-2} \sqrt{(2N+1)\,\lambda} \qquad (4.50)$$

Thus equation (4.48) can be used for predicting the excitation energy if the molecular length is known. Similarly equation (4.49) can be used for calculating the length of the molecule provided λ is known.

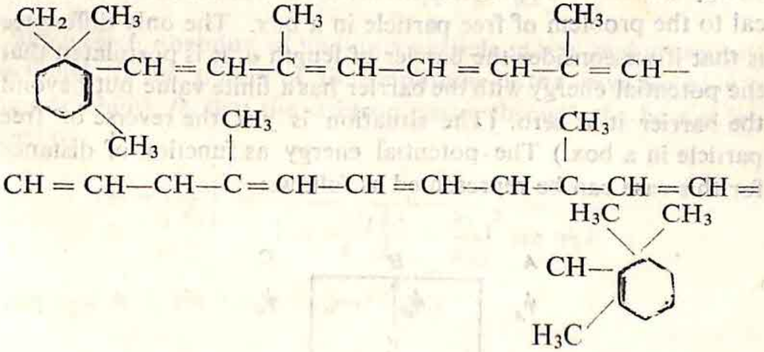
Butadiene ($2N = 4$) has an absorption maxima at 2150 Å. So that

$$l = 5.507 \times 10^{-2} \sqrt{5 \times 2130} = 5.52 \text{ Å}$$

This can be compared with the experimental value obtained by electron diffraction. The end-to-end distance is calculated in the following manner and the values are comparad in Table 4.3

Similar comparison for other polyenes has been made in Table 4.3 which shows that free electron model is a good approximation.

In the case of β-carotene found in carrots,



β-carotene (purple crystals, $mp = 184°C$)

the π-electrons are not localised in one bond but are relatively free to move throughout the whole carbon skeleton. It is easy to

Table 4.3. Test of free electron model for polyenes

	$2N$	Max. absorption Å	1 (Calc) Å	1 (direct) Å
Butadiene $CH_2{=}CH{-}CH{=}CH_2$	4	2150	5.52	3.66
Hexatriene $CH_2{=}CH{-}CH{-}CH{-}CH{=}CH_2$	6	2500	7.3	6.1
Octatriene $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$	8	2900	8.9	8.6
Vitamin A	10	3250	10.4	11.1

calculate the wavelength of the light that is absorbed by such a system using equation (4.49). The theoretical value of 4630 Å agrees well with the experimental value of (4500 Å).

APPENDIX I: TUNNEL EFFECT

Tunnel effect has importance in chemical kinetics since probability factor is related to the probability of reactants crossing the energy barrier. The problem involved in 'Tunnel effect' is identical to the problem of free particle in a box. The only difference is that if we consider the barrier of length *a*, it is postulated that the potential energy with the barrier has a finite value but beyond the barrier it is zero. (The situation is just the reverse of free particle in a box.) The potential energy as function of distance for this case can be represented as follows:

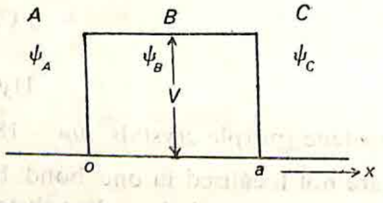


Fig. 4.8. Potential energy as a function of distance.

It means that the electron can move from A to C by crossing the energy barrier. Further $V = 0$ except for $0 \leqslant x \leqslant a$. The Schrödinger equation for the moving electron is given by

$$\frac{d^2 \psi}{dx^2} = -\frac{8\,\pi^2\, m}{h^2}\,(E - V)\,\psi$$

For the region A, the solution would yield

$$\psi_A = A_1\, e^{ik_1 x} + B_1\, e^{-ik_1 x}$$

where $k_1^2 = \dfrac{8\,\pi^2 m E}{h^2}$. Similarly for the region B where $E < V$, the Schrödinger equation would yield

$$\psi_B = A_2\, e^{k_2 x} + B_2\, e^{-k_2 x}$$

where $k_2^2 = \dfrac{8\,\pi^2 m\,(V - E)}{h^2}$. Similarly for the region C we get

$$\psi_C = A_3\, e^{-ik_1 x}$$

In the above equations, A_1, A_2, B_1, B_2 and A_3 are coefficient which can be determined by using the normalisation condition and a set of following four conditions.

$$\text{At} \quad x = 0,\ \psi_A = \psi_B,\ \frac{d\,\psi_A}{dx} = \frac{d\,\psi_B}{dx}$$

$$\text{At} \quad x = a,\ \psi_B = \psi_C,\ \frac{d\,\psi_B}{dx} = \frac{d\,\psi_C}{dx}$$

Since the probability of finding a particle in any region is proportional to the square of the amplitude of the wave function, the probability D_0 that the electron passes through the barrier is given by

$$D_0 = \left|\frac{A_3}{A_1}\right|^2 = \frac{1}{1 + \dfrac{1}{4}\left(\dfrac{k_2}{k_1} + \dfrac{k_1}{k_2}\right)^2 \sin h^2\, k_2\, a}$$

when $k_2\, a \gg 1$, $\sin h\, k_2\, a \simeq e^{k_2 a/2}$ and

$$D_0 = \left[\frac{4}{(k_2/k_1) + (k_1/k_2)}\right]^2 e^{-2k_2 a}$$

Again when $a \to \infty$, $D_0 \to 0$, the barrier is absolutely impermeable, which is the situation for particle in a box.

APPENDIX II: FREE ELECTRON MOVING IN A PERIODIC POTENTIAL

If $\psi_0(x)$ is a solution of the one-dimensional Schrödinger equation for a free electron, a solution for motion of the electron in a potential $U(x)$ that is periodic with a period a, i.e.,

$$U(x) = U(x-a) \tag{1}$$

can always be obtained in the form

$$\psi(x) = \psi_0(x)\, U(x-a) \tag{2}$$

where $U(x-a)$ itself has the same period a as the potential U. This result is called Bloch's theorem and the functions of the form (2) are called Bloch functions.

For the free electron as running waves,

$$\psi_0 = e^{ikx} \text{ where } k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h},$$

λ being the de Broglie wavelength.

Equations (1) and (2) are of considerable use in solid state Physics and Chemistry.

CHAPTER 5

Wave Mechanics of Bound Electrons—One Electron System (Hydrogen Atom and Hydrogen Atom Like Ions)

In chapter 4, we considered the case of free electron in a box or in a ring. In this chapter we will consider the case of an electron moving in a force field so that its movement is not free. The simplest example is the hydrogen atom or hydrogen atom like ions e.g., He^+, Li^{++}, Be^{+++} etc., which are two particle systems consisting of an electron of mass m and charge e and a nucleus of mass M and charge $+Ze$ where Z is the nuclear charge (Fig. 5.1). For the hydrogen atom $z = 1$.

The potential energy of the atom is entirely due to coulombic attraction between the electron and the nucleus. It is equivalent to the work done to take the electron to infinity from its instantaneous position, thus

$$V = \int_r^\infty F \cdot dr = \int_r^\infty -\frac{e^2 z}{r^2}\, dr = -\frac{e^2 \cdot z}{r} \tag{5.1}$$

where the force F has been put equal to $-\frac{z \cdot e^2}{r^2}$ where r is the distance of the electron from the nucleus. The Schrödinger equation for the above system would be given by,

$$\nabla^2 \psi_{(x,y,z)} + \frac{8\pi^2 m}{h^2}\left(E + \frac{z\, e^2}{r}\right) \psi_{(x,y,z)} = 0 \tag{5.2}$$

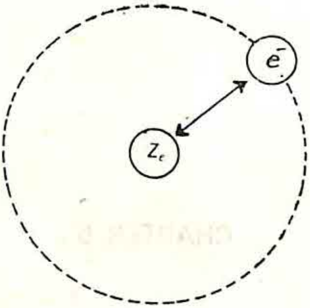


Fig. 5.1. Hydrogen atom.

In writing equation (5.2) we have considered only the motion of electron for the sake of simplicity. However hydrogen atom contains two particles, the electron (mass m) and the nucleus (mass M) and if we consider the motion of both the particle, the Schrödinger wave equation will have to be modified in appropriate manner.* Equation (5.2) is a good approximation, when we are not interested in the translational energy of the atom.

5.1 A Simple Solution of Schrödinger Equation for Hydrogen Atom

In order to solve equation (5.2) we transform the cartesian coordinates into polar coordinates according to Fig. (4.7).

Accordingly, the Schrödinger wave-equation for hydrogen atom ($z = 1$) in terms of polar coordinates can be written as (see chapter 4, p. 46)

$$\frac{1}{r^2} \cdot \frac{\partial}{\partial r}\left(r^2 \cdot \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin^2 \theta} \cdot \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \cdot \frac{\partial}{\partial \theta}$$

$$\left(\sin \theta \cdot \frac{\partial \psi}{\partial \theta}\right) + \frac{8\,\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0 \qquad (5.3)$$

If ψ depends only on r, the wave equation can be written as:

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial \psi}{\partial r} + \frac{8\,\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0 \qquad (5.4)$$

---

*Instead of the electronic mass, we have to introduce the reduced mass μ of the system given by $\mu = \dfrac{m\,M}{m + M}$.

The simplest solution of equation (5.4) is

$$\psi = e^{-ra} \qquad (e = \text{exponential})$$

where a is some arbitrary constant to be determined. The above seems to be justified since when r tends to infinity, ψ should be zero.

Since

$$\frac{\partial \psi}{\partial r} = - a\, e^{-ra} = - a\, \psi \tag{5.5}$$

and

$$\frac{\partial^2 \psi}{\partial r^2} = a^2 \cdot e^{-ra} = a^2\, \psi \tag{5.6}$$

On substituting the values of $\frac{\partial \psi}{\partial r}$ and $\frac{\partial^2 \psi}{\partial r^2}$ from equations (5.5) and (5.6) in equation (5.4) we obtain,

$$a^2 - \frac{2}{r}\, a + \frac{8\,\pi^2\, m}{h^2}\left(E + \frac{e^2}{r} \right) = 0 \tag{5.7}$$

or

$$a^2 + \frac{8\,\pi^2 m\, E}{h^2} + \frac{2}{r}\left(\frac{4\,\pi^2 m\, e^2}{h^2} - a \right) = 0 \tag{5.8}$$

Since equation (5.8) is true for any value of r, the sum of the first two terms which is independent of r and the third term involving r should be separately zero since the equation should also be satisfied when r is infinity. Thus,

$$a = \frac{4\,\pi^2 m \cdot e^2}{h^2} \tag{5.9}$$

Evidently $1/a$ is Bohr radius (cf. eq. (1.15))

and
$$E = - \frac{2\,\pi^2 m\, e^4}{h^2} \tag{5.10}$$

Since, E is negative, the electron is bound. Thus, if a and E are given by equations (5.9) and (5.10), $\Psi(r) = e^{-ra}$ is the solution to equation (5.4). $4\pi r^2 dr$ is the volume of a shell with radius r and the probability P of finding the electron in the shell would be $4\pi r^2 \Psi^2$ i.e., $4\pi r^2\, e^{-2ra}$. We can find the radius of the shell where the probability of finding the electron is maximum as follows:

since
$$P = 4\pi r^2 e^{-2ra} \tag{5.11}$$

$$\frac{dp}{dr} = [2r \cdot e^{-2ra} + r^2(-2a)e^{-2ra}]\, 4\pi \tag{5.12}$$

At the maximum,

$$\frac{dp}{dr} = 0 \tag{5.13}$$

so that

$$2r \cdot e^{-2ra} + r^2(-2a)\, e^{-2ra} = 0 \tag{5.14}$$

which leads to the result,

$$r_{\max} = \frac{1}{a} \tag{5.15}$$

In Fig. 5.2, the function $r^2 e^{-2ra}$ has been plotted against r which shows that the probability of finding the electron is maximum when $r = 1/a$ where $1/a$ is equal to Bohr's radius.

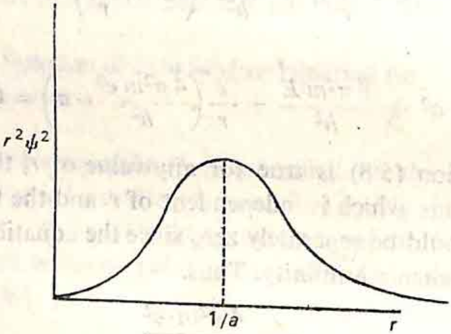


Fig. 5.2. Probability as a function of r.

5.2 Generalised Solution of Schrödinger Equation

We had assumed above that ψ only depends on r, the distance of the electron from the nucleus. In fact, this is an over simplification. We shall give below a more rigorous treatment. Equation (5.3) can be re-written as follows,

$$r^2 \cdot \left\{\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial\psi}{\partial r} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\psi\right\} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\psi}{\partial\theta}\right) = -\frac{1}{\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2} \tag{5.16}$$

we put

$$\psi_{(r\cdot\theta\cdot\phi)} = f_1 \cdot f_2 \cdot f_3 \tag{5.17}$$

where f_1 exclusively depends on r, f_2 depends only on θ and f_3 depends only on ϕ. This implies that the variables are separable. On dividing equation (5.17) by $f_1 \cdot f_2 \cdot f_3$ We obtain

$$\sin^2\theta \cdot \frac{r^2}{f_1}\left\{\frac{\partial^2 f_1}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial f_1}{\partial r} + \frac{8\,\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)f_1\right\} + \frac{\sin\theta}{f_2}\left\{\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial f_2}{\partial\theta}\right)\right\} = -\frac{1}{f_3}\cdot\frac{\partial^2 f_3}{\partial\phi^2} \tag{5.18}$$

The left hand side of equation (5.18) contains terms which are functions of r and θ only whereas the right hand side contains terms which are function of ϕ only. Equation (5.18) is true for all values of r, θ and ϕ. This is only possible when both sides are equal to a constant say m^2, so that

$$\frac{1}{f_3}\cdot\frac{\partial^2 f_3}{\partial\phi^2} = -m^2 \tag{5.19}$$

and

$$\frac{r^2}{f_1}\left\{\frac{\partial^2 f_1}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial f_1}{\partial r} + \frac{8\,\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)f_1\right\} = -\frac{1}{f_2}\left\{\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial f_2}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\right\} \tag{5.20}$$

Here again in equation (5.20), the right hand side is exclusively a function of θ and the left hand side depends only on r and the equation is true for any value of r and θ. Accordingly the two sides would be equal to a constant term α so that,

$$-\frac{1}{f_2}\left\{\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial f_2}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\right\} = \alpha \tag{5.21}$$

or

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial f_2}{\partial\theta}\right) + \left(\alpha - \frac{m^2}{\sin^2\theta}\right)f_2 = 0 \tag{5.22}$$

Equation (5.22) is a differential equation involving spherical harmonics. It is an eigenvalue equation i.e. solutions satisfying the conditions of single valuedness and continuity exist only for certain values of α. It follows that the "eigenvalues" of α are given by:

$$\alpha = l\,(l + 1) \tag{5.23}$$

so that

$$l \geqslant m \quad \text{where } l \text{ is an integer.}$$

Using relation (5.23), the equation (5.22) can be written as

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left\{\sin\theta\cdot\frac{\partial_1 P_l^m(\cos\theta)}{\partial\theta}\right\} + \left\{l(l+1)-\frac{m^2}{\sin^2\theta}\right\}P_l^m(\cos\theta)=0 \tag{5.24}$$

we have designated the eigenfunctions of equation (5.24) by the symbol $P_l^m(\cos\theta)$ as is commonly done*. We note that for a certain value of l, m can assume all values from 0 to l i.e. altogether $(2l+1)$ different values.

Now putting,

$$\frac{r^2}{f_2}\left\{\frac{\partial^2 f_1}{\partial r^2}+\frac{2}{r}\cdot\frac{\partial f_1}{\partial r}+\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)f_1\right\}=\alpha=l(l+1) \tag{5.25}$$

we get,

$$\frac{\partial^2 f_1}{\partial r^2}=\frac{2}{r}\cdot\frac{\partial f_1}{\partial r}+\left(\frac{8\pi^2 mE}{h^2}+\frac{8\pi^2 me^2}{h^2\cdot r}-\frac{l(l+1)}{r^2}\right)f_1=0 \tag{5.26}$$

or

$$\frac{\partial^2 f_1}{\partial r^2}+\frac{2}{r}\cdot\frac{\partial f_1}{\partial r}+\left(A+\frac{2B}{r}+\frac{C}{r^2}\right)f_1=0 \tag{5.27}$$

where

$$A=\frac{8\pi^2 mE}{h^2},\ B=\frac{4\pi^2 me^2}{h^2},\ C=-l(l+1)$$

---

*If P_l^m is the associated Legendre function of degree l and order the solution of θ equation is put as

$$f_2(\theta)=\sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}}\,P_l^{|m|}\cos\theta$$

The solution of equation (5.27) has to be expressed in the form of Laguerre equation and its normalised solution is

$$f_1(r)=-\sqrt{\left(\frac{2z}{na_0}\right)^3\left[\frac{(n-l-1)}{2n\{(n+l)!\}^3}\right]}\,e^{-p}{}_{2}\,p^l L_{n+l}^{2l+1}(p)$$

where $p=(2z/na_0)r$, $a_0=\dfrac{h^2}{4\pi^2 m^2}$ and $L_{n+l}^{2l+1}(p)$ represents the associated Laguerre polynomial.

The acceptable solutions of equation (5.27) are obtained when $B^2 = -n^2 A$, where n is an integer, so that

$$E = \frac{-2\pi^2 me^4}{n^2 h^2} (n = 1, 2, 3, \ldots) \qquad (5.28)$$

It further follows that for acceptable solution

$$n \geqslant l + 1$$

i.e.,

$$l = 0, 1, 2, 3, \ldots (n-1)$$

which is in agreement with the semi-empirical condition for the quantum number l obtained on the basis of hydrogen spectra.

Summarising, we find that the quantum numbers n and 1 have to be introduced in order to obtain acceptable solutions for stationary states of electrons. Similarly, it is found that the function f_3 will yield acceptable solutions when m, the magnetic quantum number has the values $0, \pm 1, \pm 2 \ldots$ etc. The proof of this is as follows:

Since equation (5.19) is a second order differential equation, the solution is given by

$$f_3 = C\, e^{\pm im\phi} \qquad (5.29)$$

where C is the constant of integration. On account of the normalisation condition

$$\int_0^{2\pi} f_3^2 \, d\phi = 1 \qquad (5.30)$$

i.e.

$$\int_0^{2\pi} C^2 e^{\pm 2\, i\, m\phi} \, d\phi = 1$$

or

$$C^2 \int_0^{2\pi} d\phi = 1$$

or

$$C = \frac{1}{\sqrt{2\pi}}.$$

The final normalised wave function is

$$f_3 = \frac{1}{\sqrt{2\pi}} \cdot e^{\pm im\phi}$$

where

$$m = 0, \pm 1, \pm 2, \ldots$$

We further note that for each value of m in the function f_3, the function f_2 will yield acceptable solution only if a second number is introduced which is called l. The second number is always positive and must not be numerically less than m. Subsequent analysis shows that for each combination of m and l, Schrödinger equation will yield acceptable solutions only when a third whole number is introduced which must not be less than l.

Thus
$$m = 0, \pm 1, \pm 2, \pm l$$
$$l \geqslant m$$
$$n \geqslant l + 1$$

Thus, by writing the wave-equation in polar coordinates, solution for hydrogen atom can be obtained only by the introduction of three whole numbers. Each combination of these whole numbers correspond to a definite electronic state. These three whole numbers n, l and m constitute the three main quantum numbers specifying the state of the electron in the hydrogen atom. It should be noted that we get three unique quantum numbers on account of three independent differential equations associated with r, θ and ϕ.

In order to account for the fine structure of atomic spectra and the magnetic properties of atoms with zero orbital angular momentum an additional quantum number s has been introduced. It is called spin quantum number and has a value $\pm 1/2$. Its existence has been justified on the basis of relativistic wave mechanics. The wave mechanics introduces the three quantum numbers not as arbitrary assumptions but as the result of inevitable conditions which must be satisfied if the equations are to yield acceptable solutions.

The complete solution of equation (5.2) is summarised in Table 5.1.

The allowed values of quantum numbers and the properties of the orbital with which these are associated are given in Table 5.2.

In quantum mechanics, we do not use the term orbit, since the electron moves throughout the volume rather than along a curve of a fixed orbit. To emphasise this difference, we say that the particle moves in an orbital described by ψ-function.

Table 5.1. The hydrogen atom wave function $\psi = f_1(r) f_2(\theta) f_3(\phi)$ for $n = 1$ and $n = 2$ shells

($a_0 = 0.529$A, Z = effective nuclear charge for $H = 1$)

n	l	m	$f_1(r)$	$f_2(\theta) f_3(\phi)$	Wave function symbol
1	0	0	$2\left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$	$\left(\frac{1}{4\pi}\right)^{1/2}$	1s
2	0	0	$\left(\frac{z}{2a_0}\right)^{3/2}\left(2-\frac{zr}{a_0}\right) e^{-zr/2a_0}$	$\left(\frac{1}{4\pi}\right)^{1/2}$	2s
2	1	0	$\frac{1}{\sqrt{3}}\left(\frac{z}{2a_0}\right)^{3/2}\left(\frac{zr}{a_0}\right) e^{-zr/2a_0}$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$	$2p_z$
2	1	+1	$\frac{1}{\sqrt{3}}\left(\frac{z}{2a_0}\right)^{3/2}\left(\frac{zr}{a_0}\right) e^{-zr/2a_0}$	$\left(\frac{3}{4\pi}\right)\sin\theta\cos\phi$	$2p_x$
2	1	−1	$\frac{1}{\sqrt{3}}\left(\frac{z}{2a_0}\right)^{3/2}\left(\frac{zr}{a_0}\right) e^{-zr/2a_0}$	$\left(\frac{3}{4\pi}\right)\sin\theta\sin\phi$	$2p_y$

Table 5.2. Allowed values of quantum numbers

Symbol	Name	Allowed values	Property principally determined
n	Principal	1, 2, 3, ...	Size and energy of orbital
l	Azimuthal	0. 1, 2 . . . . $n-1$,	Shape of orbital
n	Magnetic	$-l, -l+1, \ldots$ 0, 1, 2 . . . l	Orientation of orbital
S	Spin	$+\frac{1}{2}, -\frac{1}{2}$	Spin of electron

5.3 Pictorial Interpretation of Wave-functions

Since ψ is a function of three variables r, θ and ϕ, it is not possible to have a three-dimensional plot. Hence a pictorial idea of wave-function is impossible. However, we can have three-dimen-

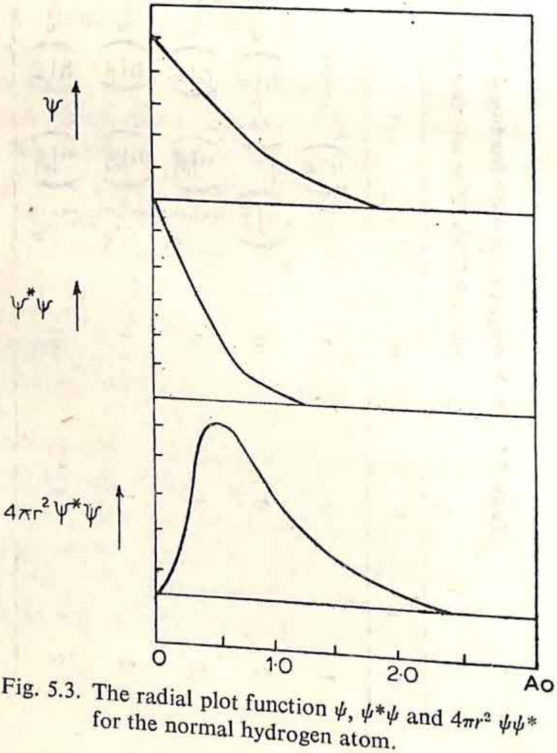


Fig. 5.3. The radial plot function ψ, $\psi^*\psi$ and $4\pi r^2\ \psi\psi^*$ for the normal hydrogen atom.

sional plot by keeping r constant or a two-dimensional plot by keeping either (i) θ and ϕ constant, (ii) r and ϕ constant, or (iii) r and θ constant. For case (i) one may plot ψ against r or ψ^2 the probability density against r or probability $4\pi r^2\psi^2$ against r. A typical plot for 1*s* orbital is shown in Fig. 5.3. Similar plot for other orbitals are shown in Fig. 5.4.

The units on the ordinate scale are different for ψ^2 and $4\pi r^2\psi^2$.

It should be noted that Figs. 5.3 and 5.4 do not give any idea about the shape of the orbital. In this respect, a plot of angular variation of orbitals is more meaningful which are described in Fig. 5.5 (a, b, c) for *p*, *d* and *f* orbitals.

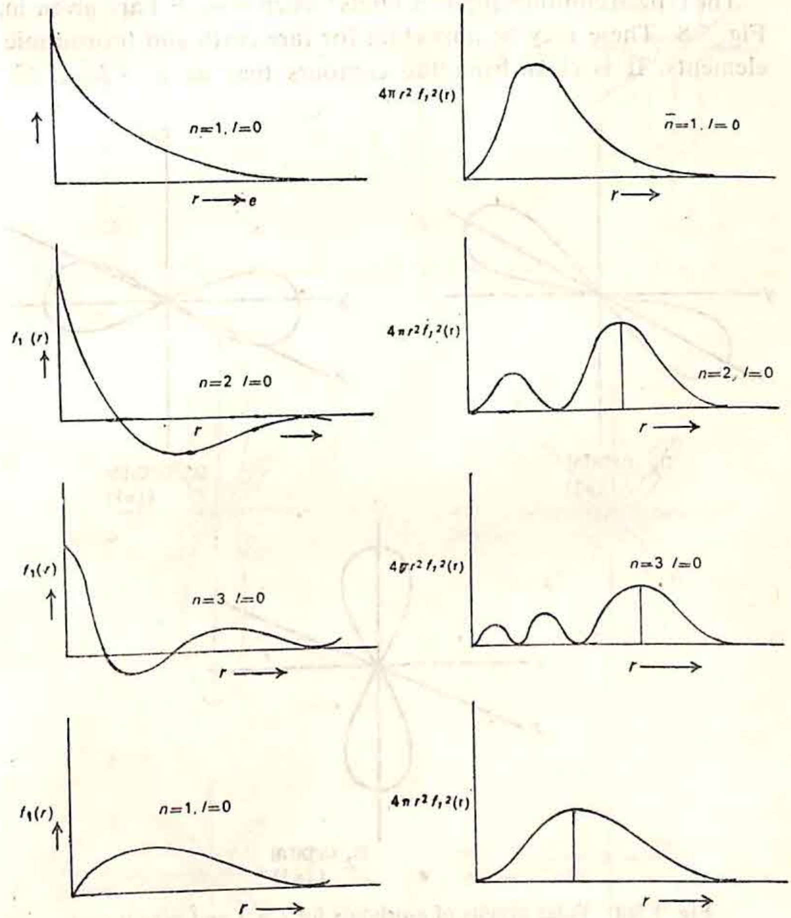


Fig. 5.4. Radial and probability distribution function of various orbitals.

Since the probability density is greatest at $r = 0$ and falls rapidly as one moves from the nucleus, we can represent 1*s* orbital pictorically as in Fig. 3.2 where density of dots is a measure of electron density.

5.4 Contour Diagrams

Another alternative way which is better in many respects is to define the character of the orbital in terms of contours of definite value of $\psi^2/\psi^2_{\max}$. Such contours for *p*, *d*, and *f* have been drawn in Figs. 5.6-5.8.

The typical contours for 4*f* orbitals* when $m = \pm 1$ are given in Fig. 5.8. These may be important for rare earth and transuranic elements. It is clear from the contours that as $\psi \to \psi_{\max}$, $\psi^2/$

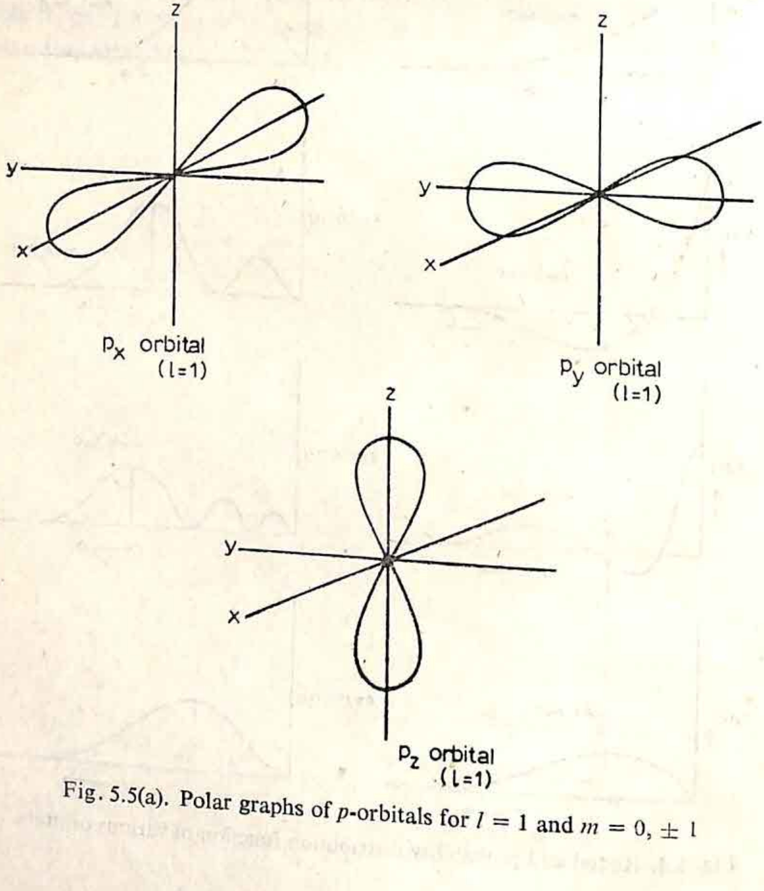


Fig. 5.5(a). Polar graphs of *p*-orbitals for $l = 1$ and $m = 0, \pm 1$

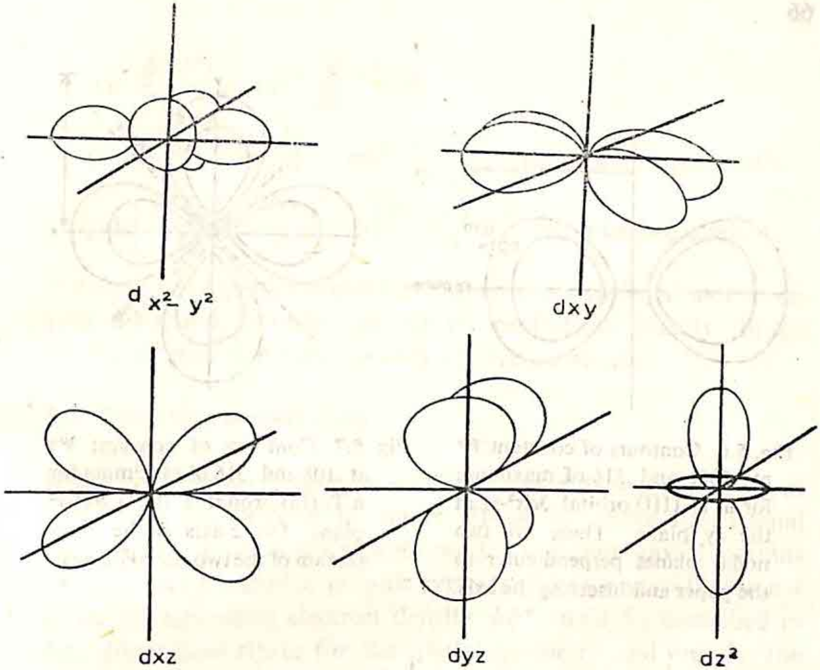


Fig. 5.5(b). Polar graphs of *d*-orbitals for $l = 2$ and $m = 0, \pm 1, \pm 2$.

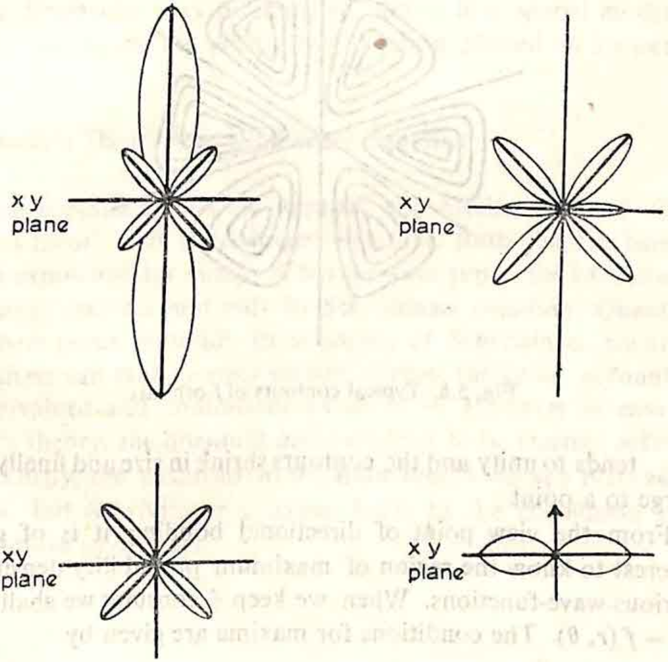


Fig. 5.5(c). Polar graphs of *f*-orbitals for $l = 3$ and $m = 0, \pm 1, \pm 2$ and ± 3.

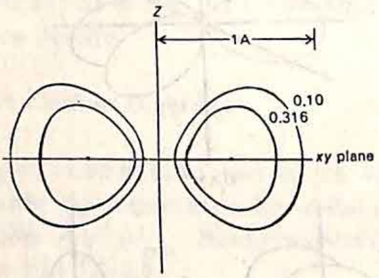


Fig. 5.6. Contours of constant Ψ^2 at .108. and .316 of maximum for a Ti (III) orbital $3dx^2$-y^2 in the xy plane. There are two nodal planes perpendicular to the paper and bisecting the axis.

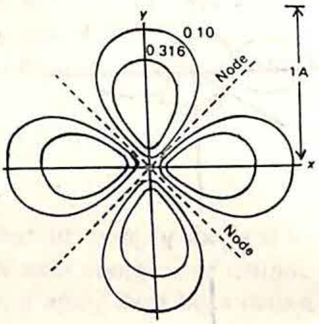


Fig. 5.7. Contours of constant Ψ^2 at .108 and .316 of maximum for a Ti (iii) orbital is the 3 dx^2-y^2 plane. The z-axis is the intersection of the two nodal planes.

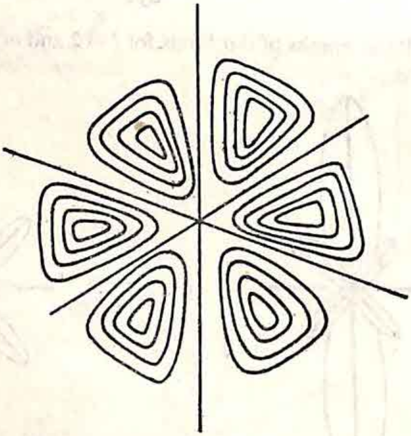


Fig. 5.8. Typical contours of f-orbitals.

ψ^2_{max} tends to unity and the contours shrink in size and finally converge to a point.

From the view point of directional bonding it is of grater interest to know the region of maximum probability density for various wave-functions. When we keep ϕ constant we shall have $\psi^2 = f(r, \theta)$. The conditions for maxima are given by

(i) $\frac{\partial\,(\psi^2)}{\partial r} = 0;\ \frac{\partial\,(\psi^2)}{\partial \theta} = 0$

(ii) $\frac{\partial^2\,(\psi^2)}{\partial r^2},\ \frac{\partial^2\,(\psi^2)}{\partial \theta^2}$ and $\frac{\partial^2\,(\psi^2)}{\partial r\,\partial \theta}$ are negative quantities

(iii) $\left[\frac{\partial^2\,(\psi^2)}{\partial r^2}\cdot\frac{\partial^2\,(\psi^2)}{\partial r^2} - \left(\frac{\partial^2\,(\psi^2)}{\partial r\,\partial \theta}\right)\right]$ is a positive quantity.

We shall have similar conditions, when ψ is expressed as a function of r and ϕ. It turns out that the probability density for *2p*, *3d* and *4f* state is maximum only at specific points.

5.5 Three-dimensional Plots

It has been stated in section 5.3 that three-dimensional plots of ψ-function are difficult to obtain. However, three-dimensional plots have been accurately produced for different wave functions by computer controlled graphic systems. Since a wave function ψ or its corresponding electron density $\psi\psi^*$ must be described in four dimensions (three for the spatial geometry and one for the point-by-point value of the function), any three-dimensional plot would leave out some information; buy yet no more than three dimensions may be depicted clearly in a spatial model or in its corresponding perspective diagram plotted on a sheet of paper.

5.6 Bohr's Theory and Schrödinger Equation

Before concluding, let us compare the results obtained from Bohr's theory and Schrödinger equation. Both theories lead to same expression for energy E but the wave properties of electrons are taken into account only by Schrödinger equation. Quantum numbers occur naturally in solutions of Schrödinger equation and these can take up only certain integral values on account of single-valued and continuous nature of ψ. However in case of Bohr's theory, the quantum numbers have to be inserted arbitrarily. Lastly, the electrons in the Bohr theory occupy planet-like orbits, but Schrödinger equation leads to the conclusion that these move in orbitals.

CHAPTER 6

Polyelectronic Atoms

In Chapter 3, we discussed the solution of Schrödinger equation for hydrogen and hydrogen-like atoms. This solution will not be valid for a two electron or many electron systems. This is because ψ would then be a function of $3N$ cordinates (where N = number of extra-nuclear electrons) and the potential energy would include terms on account of electron-electron repulsion also.

6.1 Helium Atom

We will consider the simplest case provided by the helium atom or Helium like atoms containing two electrons. Examples of the latter are H^-, Li^+, Be^{++} etc., where the nuclear charge is + Ze. In Fig. 6.1 the electrons are numbered 1 and 2 the polar coordinates for which are r_1, θ_1, ϕ_1 and r_2, θ_2, ϕ_2 respectively. The

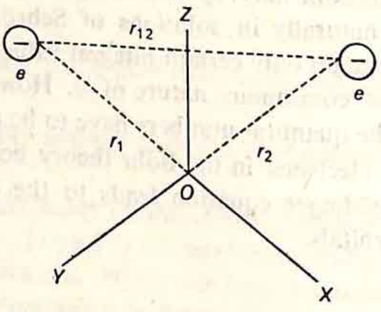


Fig. 6.1. He atom or He-like ions.

Schrödinger equation for the present case can be written as

$$\nabla_1^2\psi + \nabla_2^2\psi + \frac{8\,\pi^2 m}{h^2}\left(E + \frac{ze^2}{r_1} + \frac{ze^2}{r_2} - \frac{e^2}{r_{12}}\right)\psi = 0 \quad (6.1)$$

where r_1 and r_2 are the distances of the electron 1 and 2 from the nucleus and r_{12} is the distance between the electrons 1 and 2. The inclusion of term containing r_{12} in equation (6.1) makes the solution of the equation difficult since we cannot solve it by putting,

$$\psi = f_1(r_1, \theta_1, \phi_1) \cdot f_2(r_2, \theta_2, \phi_2) \quad (6.2)$$

because the variables cannot be separated.

On account of these difficulties, approximate methods had to be used for solving equation (6.1). These methods are,

i) Perturbation method.
ii) Variation method.

Since Helium ion (He$^+$) resembles the hydrogen atom with the difference that the charge Z on the nucleus is twice as great as that of hydrogen atom, the wave function for ground state 1*s* can be written as,

$$\psi_1 = 2\left(\frac{1}{4\pi}\right)^{1/2}\left(\frac{2}{a_0}\right)^{3/2} e^{-2r/a_0} \quad (6.3)$$

$$= \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{3/2} e^{-2r/a_0} \quad (6.4)$$

The energy E_{He^+} of the helium ion is then found to be given by

$$E_{\mathrm{He}^+} = -\frac{4\cdot 2\cdot\pi^2 me^4}{n^2h^2} = -4E_H \quad (6.5)$$

where E_H is the energy of the hydrogen atom. The energy of the unperturbed helium atom E_0 when electron-electron repulsion is neglected, can be shown to be equal to twice the energy of He$^+$ i.e. $-8E_H$. This value is very much higher than the experimental value of the energy of helium atom which is found to be $-5.8\ E_H$.

The above analysis leads to the conclusion that interaction between two electrons must be taken into account. In order to have a more realistic solution of the problem, we shall first discuss the perturbation method.

6.2 Perturbation Method

We would treat the repulsion potential in the helium atom as the perturbation V' given by

$$V' = +\frac{e^2}{r_{12}} \tag{6.6}$$

where r_{12} is the distance between electrons 1 and 2.

Accordingly, the mean energy is different from the unperturbed value by an amount E' which can be calculated (see Chapter 3, section 3.4) from the following formula

$$E' = \iint \frac{e^2}{r_{12}} (N \cdot e^{-2r_1/a_0})^2 \, (N \cdot e^{-2r_2/a_0})^2 \, d\tau_1 \, d\tau_2 \tag{6.7}$$

where $d\tau_1$ and $d\tau_2$ are the volume elements corresponds to electrons 1 and 2, where N is the normalising factor. However, if the unperturbed wave function is used in the form,*

$$\psi_0 = e^{-2r_1/a_0} \cdot e^{-2r_2/a_0} \tag{6.8}$$

which is not normalised, the expression for the perturbation energy would be given by

$$E' = \frac{\displaystyle\iint \frac{e^2}{r_{12}} (e^{-2r_1/a_0} \cdot e^{-2r_2/a_0})^2 \, d\tau_1 \, d\tau_2}{\displaystyle\iint (e^{-2r_1/a_0} \cdot e^{-2r_2/a_0})^2 \, d\tau_1 \, d\tau_2} \tag{6.9}$$

The evaluation of the integral yields,

$$E' = \tfrac{5}{2} \cdot E_H \tag{6.10}$$

It may be noted that the value of E' is positive. This is so because the repulsion between electrons lowers the energy of the helium atom. This result can be generalised for any system with a nuclear charge Z such as H^-, Li^+, Be^{++}, B^{+++}. For a general case, E' is given by

$$E' = \tfrac{5}{4} \cdot Z \cdot E_H \tag{6.11}$$

Thus, the energy of the helium atom would be given by

$$E = E_0 + E' = -8\, E_H + \tfrac{5}{2} \cdot E_H = -5.5\, E_H \tag{6.12}$$

This may be compared with the experimental value of $-5.8\, E_H$. Since the first ionisation potential is the energy required to remove one electron, first ionisation potential = energy of the helium atom—energy of the second electron so that,

---

*The factor 2 occurs in equations (6.7) and (6.8) on account of this fact that the nuclear charge on the helium atom is 2.

$$\text{I.P.} = -5.5\,E_H - (-4\,E_H) = -1.5\,E_H \qquad (6.13)$$

The experimental value of ionisation potential is 1.8 E_H. Thus, the agreement between theory and experiment is impressive. These values are recorded in Table 6.1.

Table 6.1. Energy and ionisation potential of He atom

Parameters	Theoretical value for unperturbed case	Theoretical value based on perturbation theory	Theoretical value by variation theory	Experimental value
1. Energy	$-8\,E_H$	$-5.5\,E_H$	$-5.7\,E_H$	$-5.8\,E_H$
2. Ionisation potential	$-4\,E_H$	$-1.5\,E_H$	$-1.71\,E_H$	$-1.8\,E_H$.

6.3 Variation Method

We now discuss an alternative method for the solution of equation (6.1). This involves the choice of a proper, trial function. The unperturbed function used in the previous method was a simple wave function for a nuclear charge of 2. Inter-electron repulsion will result in an expansion of the electron cloud. On account of the presence of other electron it would effectively mean that the nuclear charge is rather less than 2. In other words, the other electron screens some of the nuclear charge. This suggests that it would be more realistic to replace e^{-zr/a_0} by $e^{-z'r/a_0}$ where $z' \neq z$. Accordingly the perturbation energy E' would be given by

$$E' = \frac{\iint (e^{-z'r_1/a_0} \cdot e^{-z'r_2/a_0}) \cdot H \cdot (e^{-z'r_1/a_0} \cdot e^{-z'r_2/a_0})\, d\tau_1\, d\tau_2}{\iint (e^{-z'r_1/a_0} \cdot e^{-z'r_2/a_0})(e^{-z'r_1/a_0} \cdot e^{-z'r_2/a_0})\, d\tau_1\, d\tau^2} \qquad (6.14)$$

where

$$H = -\frac{h^2}{8\,\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \qquad (6.15)$$

On solving integrals in equation (6.14), we have

$$E' = [-2z'^2 + \tfrac{5}{4}\,z' - z'\,(\tfrac{5}{16})^2]\,E_H \qquad (6.16)$$

The minimum value of E' is found by differentiating E' with Z' and putting $\partial E'/\partial Z' = 0$ which yields $Z' = 27/16$. When this value of Z' is substituted in equation (6.16) E is found to be $-5.7\,E_H$ which is excellent agreement with the experimental value. Thus the error in the total energy has now been reduced to about 1.7%. Similarly it is found that the error in the calculated ionisation potential is only about 5%. The wave function which minimises the energy corresponds to an effective nuclear charge which is 5/16 less than the nuclear charge Z.

This is true H^-, Li^{++}, Be^{++} etc. also. Hylleras carried out intensive work on the ground state of the helium atom. He used variation functions of the type

$$e^{-z'r_1/a_0} \cdot e^{-z'r_2/a^0} \{1 + f(r_1, r_2, r_{12})\}$$

and

$$e^{-z'r_1/a_0} \cdot e^{-z'r_2/a_0} \left\{1 + \frac{e\,(r_1 - r_2)^2}{a_0^2}\right\}$$

In the latter case there are two constants Z and C, the values of which were found by minimising the energy i.e. by putting $\dfrac{\partial \psi}{\partial z} = 0$ and $\dfrac{\partial \psi}{\partial c} = 0$. The values were $z = 1.69$ and $c = 0.142$. The calculated value of the energy was found to be 1% of the true value. Hylleras also used another function

$$e^{-z'r_1/a_0} \cdot e^{-z'r_2/a_0} \left(1 + c' \cdot \frac{r_{12}}{a_0}\right)$$

which gave energy within 0.4% of the true value. He obtained a general formula for the ionisation energy I of the helium atom and helium like-ions given by

$$I = \frac{R\,he}{1 + \dfrac{m}{M}} \left(z^2 - \frac{5}{4}z + 0.31488 - \frac{0.01752}{z} + \frac{0.00548}{z^2}\right) \quad (6.17)$$

where

$$R = 109737.42 \text{ cm}^{-1}$$

and M is the atomic mass. The calculated values using equation (6.17) are compared with the experimental values in Table 6.2. More refined treatments of helium atom have been proposed which are due to Taylor and Parr (1952), Lennard-Jones (1952) and Mulliken (1952).

Table 6.2. **Ionisation energies of two-electron atoms**

Atom	I (Calculated) e.v.	I (Observed) e.v.
H	0.7149	—
He	24.465	24.463
Li^{+}	75.257	75.279 ± 0.012
Be^{++}	153.109	153.09 ± 0.10
B^{+++}	258.029	258.1 ± 0.2
C^{4+}	390.020	389.9 ± 0.4

6.4 Elements Other than Hydrogen and Helium

Many electron system is a little more complicated than the previous case since following types of interaction can occur,

1) Interaction of inner shell-electrons with each other,
2) Interaction of inner shell-electrons with outer electrons, and
3) Interaction of outer (valence shell) electrons with each other.

In calculating the energies of the atom beyond helium, we may start as in the case of helium by neglecting the terms in the Hamiltonian that represent the electrostatic repulsions of the electrons. This leads to a partial differential equation of the type,

$$\sum_{i=1}^{N} \Delta_i^2\psi + \frac{8\,\pi^2 m}{h^2}\left[E + \sum_{i=1}^{N} \frac{zc^2}{r_i}\right]\psi = 0 \tag{6.18}$$

N is the number of electrons in the atom Δ_i^2 is the Laplacian of the ith electron and r_i is its distance from the nucleus. This equation can be solved by the method of separation of variables by writing the total wave function as the product of wave function of the individual electrons, so that

$$\psi = \prod_{i=1}^{N} \phi\,(n_i, l_i, m_i, s_i)_i$$

where n_i, l_i, m_i, and s_i are the four quantum numbers assigned to the ith electron and $\phi\,(n_i, l_i, m_i, s_i)_i$ is the corresponding hydrogen-like orbital arising from nuclear charge z. In the perturbation treatment of polyelectronic atoms, we again use the hydrogen-like orbitals. Since the perturbation treatment is complicated we shall not give the details. Instead we shall discuss merely the outline.

In case of helium atom, we have seen that because of the icreening effect of electrons on each other, the true wave functions are much less concentrated about the nucleus than would be expected from the hydrogen-like wave functions in which all electronic repulsion are neglected. By replacing the true nuclear charge z, in the exponential term of the hydrogen-like orbitals with an effective nuclear charge $z' = z - s$ the orbitals can be made to spread about, away from the nucleus, and thus we would get a better representation of true wave-function. The constant is known as screening constant and its value would be expected to vary from one orbital to another. It is, in effect the average number of electrons spending their time in the given region between the given orbital and the nucleus.

Using this approach, Zener and Slater have set up simplified atomic orbitals that are widely used in making quantum mechanical calculations. They showed that for many purposes only the term with the highest power of r in $f_1(r)$ is of importance. Therefore, they wrote the orbitals in the form

$$\psi = r^{n^*-1}\, e^{-(z-s)r/n^*}\, f_1(\theta) \cdot f_2(\phi) \tag{6.20}$$

where the constants n^* and s are chosen according to certain rules as given in Table 6.3.

Table 6.3. Parameters of Slater orbitals

Orbital	s	n	n^*
1s	0.30	1	1
2s or 2p	4.15	2	2
3s or 3p	10.25	3	3
4s	23.15	4	3.7
3d	19.75	5	4.0
		6	4.2

This system of selecting s and n was developed so as to give the best possible fit to the observed energies and size of atoms. The screening constant s for each electron is calculated as follows:

1) The electrons are divided into groups in the following order i.e. 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p etc.

2) For each electron in a given group, the screening constant is the sum of the following contributions,

a) No contribution from any group outside the given group.

b) A contribution amounting to 0.35 from each electron in the given group except $1s$, for which 0.30 per electron is used.

c) In the case of s, p sub-shells, contribution amounting to 0.85 from each electron whose principal quantum number is less by one and 1.00 from each electron further in is considered. However, if the given group is d or f, contribution amounting to 1.00 from each and every inner electron is taken into account.

As an exmaple, for carbon ($1s^2\,2s^2\,2p^2$) with $z = 6$ we have effective z for $1s$ electron $= 6 - 0.30 = 5.70$ and effective z for $2s$ and $2p$ electrons $= 6 - (3 \times 0.35) - (2 \times 0.85) = 3.25$.

6.5 Hartree Self-consistent Field Method

Slater-Zener orbitals are approximate. A more rigorous way for writing the orbitals was developed by Hartree and Fock.

We write the wave function ψ of an atom containing N electrons in the following form of a product of one electron orbitals,

$$\psi = \phi_1^{(1)}\,\phi_2^{(2)} \,\ldots\, \phi_N^{(N)}$$

where $\phi_1, \phi_2 \ldots . \phi_N$ are the respective orbitals, ψ would be a function of $3N$ co-ordinates associated with N electrons, $\phi_1^{(1)}$ would be a function of the coordinates of electron 1 and $\phi_2^{(2)}$, $\phi_3^{(3)}$, etc. would have similar significance. Hartree has developed an interesting method of deducing orbitals that will make the function ψ give the best possible representation of the correct wave function of the atom.

The quantity $\phi_1^2\,(1)$ represents the probability density of electron 1 in the atom, and similarity $\phi_2^2\,(2)$ represents the probability density of electron 2 and so on. If the electron 1 is placed at a definite point in space, with coordinates x, y, z, then the average electrostatic interaction between electrons 1 and 2 is given by

$$V_1\,(x_1, y_1, z_1) = \iiint \frac{e^2\,\phi_2^2\,(2)}{r_{12}}\,dx_2\,dy_2\,dz_2 \tag{6.21}$$

where the integral is to be taken over all positions of electron 2. Similar contributions to the potential energy of electron 1 are made by each of the other electrons in the atom. In general the total potential energy of the electron j can be written as,

$$V_j\,(x_j, y_j, z_j) = -\frac{ze^2}{r_j} + \sum_{i \neq j} \frac{e^2\,\phi_i^2\,(i)}{r_{ij}}\,dx_i\,dy_i\,dz_i \qquad (6.22)$$

The first term on the right is the potential energy due to attraction between electron and the nucleus. Equations similar to (6.22) can be written for the potential energy of the other electrons also.

The wave function of the electron moving in the potential field is given by the solution of Schrödinger equation using atomic units,

$$-\frac{h^2}{8\pi^2 m}\nabla_j^2\phi_j + V_j\phi_j = E_j\phi_j \qquad (6.23)$$

where E_j is the energy of the electron in orbital ϕ_j. It is clear that equation (6.23) cannot be solved until equation (6.22) has been evaluated and we cannot solve equation (6.22) until we know the solutions ϕ_j from equation (6.23). This vicious circle may be broken by making a preliminary reasonable assumption regarding the ψ-function in equation (6.23). For instance, we might use Slater orbital and evaluate V_j. The resulting potentials V_j may then be used to find improved wave-function by again using equation (6.23). The improved wave-function may again be introduced in equation (6.22) to obtain an improved estimate of the potential function V_j. The process may be repeated until the functions ϕ_j do not change appreciably. The resulting potential function V_j is then said to be the self-consistent field and the resulting wave-function is called self-consistent field orbital. The total energy of the atom or ion would be the sum of the energies of individual electrons so that

$$E = \sum_{j=1}^{N} E_j \qquad (6.24)$$

where the E_j's are the eigenvalues of the equation (6.23).

The basic features of Hartree-Fock SCF approach may be summarised as follows:

(i) The orbital concept is assumed to be valid.

(ii) A set of reasonable orbitals is arbitrarily selected.

(iii) We calculate the effect of all the other electrons on one of the electrons. We do this in turn for each orbital, thus obtaining a set of first improved orbitals. The calculations are then repeated with the first improved orbital to obtain a set of second improved orbital. The process is then continued until no further significant improvement is obtained; the orbitals are then self-consistent.

Hartree-Fock SCF orbitals are probably the best that have been obtained uptil now within the limitations of orbital concept. These correctly predict the energy of the system to within one or two per cent of the observed value. The SCF orbitals have been applied to numerous atoms and ions. Fock has shown that Hartree's method may be modified to take into account the exchange between orbitals.

6.6 Energy States of Hydrogen-like Atoms and Polyelectronic Atoms

According to equation (5.28) the energy of the electron in hydrogen-like atom is determined only by the quantum number n. Accordingly the order of energy levels will be as follows,

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < 5s$$

which gives several degenerate energy levels. However, the orbital degeneracy can be removed by considering the effect of electron-electron repulsion and the sequence of energy levels is found to be as shown in Fig. 6.2.

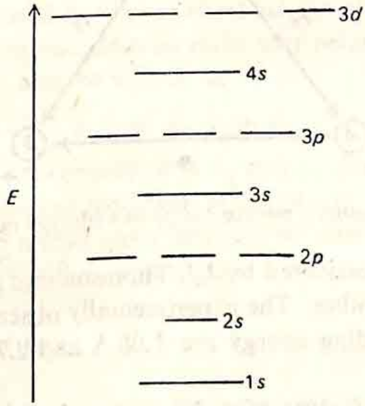


Fig. 6.2. Orbital energies in complex atoms.

CHAPTER 7

Small Molecules

7.1 Hydrogen Molecule Ion

In chapter 6 we have investigated the quantum mechanics of a system containing electrons and a single nuclear charge. We will now study a slightly different situation when the electrons move in a force field due to two or more nuclei. We consider the simplest system H_2^+ having two nuclei A and B and one electron which may formally be represented as follows.

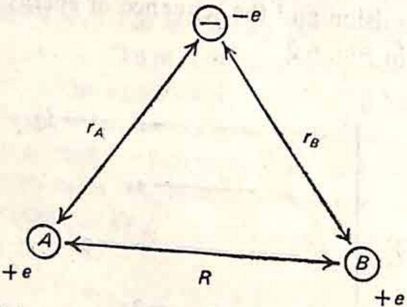


Fig. 7.1. Schematic representation of hydrogen molecule ion.

H_2^+ was first discovered by J.J. Thomson and is known to exist in gas discharge tubes. The experimentally observed internuclear distance and binding energy are 1.06 Å and 2.791 eV respectively.

The important feature of such a system is that:

i) there is attraction between electron and the nuclei, and

ii) there is repulsion between the nuclei A and B.

Accordingly the Hamiltoman for the system would be written as follows:

$$H = -\frac{h^2}{8\pi^2_m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \tag{7.1}$$

where the nuclear charge on A and B is $+e$ and R is the internuclear distance. r_A and r_B are the distances of the electorn from nuclei A and B respectively.

Since the binding energy and internuclear distance for the hydrogen molecule ion are known from experiment, the object of the quantum mechanical calculation is to evaluate these two parameters from theory based on a particular picture of molecular binding. Accordingly we shall evaluate E, ψ and ψ^2 for the system. As shown earlier in chapter III, E can be easily evaluated from the following expression provided a suitable trial wave function ψ can be suggested,

$$E = \frac{\int \psi\, H\, \psi^*\, d\tau}{\int \psi\, \psi^*\, d\tau} \tag{7.2}$$

The simplest way to guess the wave function is to argue as follows. If the nuclei are far apart, the system can be considered as $H_A + H_B^+$ or $H_B + H_A^+$ where the subscripts A and B refer to the two nuclei. Since the two hydrogen atoms and the two hydrogen ions cannot be distinguished, the simplest wave function for the system would be a linear combination of respective atomic orbitals. Thus, the one electron molecular orbital for the hydrogen molecule ion may be written as

$$\psi = a_1\, \psi_a + a_2\, \psi_b \tag{7.3}$$

where a_1 and a_2 are constant and ψ_a and ψ_b denote, the ground state atomic orbitals of hydrogen atoms A and B.

Having chosen a trial wave function we now proceed with the evaluation of (i) E, (ii) ψ, and (iii) ψ^2.

7.2 Evaluation of E

On substituting the value of ψ from equation 7.3 in equation (7.2) we have,

$$E = \frac{\int (a_1 \psi_a + a_2 \psi_b) H (a_1 \psi_a^* + a_2 \psi_b^*) \, d\tau}{\int (a_1 \psi_a + a_2 \psi_b)(a_1 \psi_a^* + a_2 \psi_b^*) \, d\tau} \tag{7.4}$$

or

$$E \left[\int (a_1 \psi_a + a_2 \psi_b)(a_1 \psi_a^* + a_2 \psi_b^*) \, d\tau \right] = \int (a_1 \psi_a + a_2 \psi_b) H (a_1 \psi_a^* + a_2 \psi_b^*) \, d\tau \tag{7.5}$$

or

$$E \left[\int a_1^2 \psi_a \psi_a^* \, d\tau + 2a_1 a_2 \int \psi_a \psi_b^* \, d\tau + \int a_2^2 \psi_b^* \psi_b \, d\tau \right] = \left[a_1^2 \int \psi_a H \psi_a^* \, d\tau + 2 a_1 a_2 \int \psi_a^* H \psi_b \, d\tau + a_2^2 \int \psi_b^* H \psi_b \, d\tau \right] \tag{7.6}$$

For a minimum value of E, we should have,

$$\frac{\partial E}{\partial a_1} = 0 \tag{7.7}$$

$$\frac{\partial E}{\partial a_2} = 0 \tag{7.8}$$

Using equations (7.6) and (7.7) we have,

$$E \left[2a_1 \int \psi_a^* \psi_a \, d\tau + 2a_2 \int \psi_a^* \psi_b \, d\tau \right] + \frac{\partial E}{\partial a_1} \left[\int a_1^2 \psi_a \psi_a^* \, d\tau + 2a_1 a_2 \int \psi_a \psi_b^* \, d\tau + \int a_2^2 \psi_b \psi_b^* \, d\tau \right] = 2a_1 \int \psi_a H \psi_a^* \, d\tau + 2a_2 \int \psi_a^* H \psi_b \, d\tau \tag{7.9}$$

or

$$E \left[2a_1 \int \psi_a^* \psi_a \, d\tau + 2a_2 \int \psi_a^* \psi_b \, d\tau \right] = 2a_1 \int \psi_a^* H \psi_a \, d\tau + 2a_2 \int \psi_a^* H \psi_b \, d\tau \tag{7.10}$$

Equation (7.9) can be put in the following form,

$$E[2a_1 S_{aa} + 2a_2 S_{ab}] = 2a_1 H_{aa} + 2a_2 H_{ab} \tag{7.11}$$

where

$$S_{aa} = \int \psi_a^* \psi_a \, d\tau$$

$$S_{ab} = \int \psi_a^* \psi_b \, d\tau$$

$$H_{aa} = \int \psi_a^* \, H \, \psi_a \, d\tau$$

$$H_{ab} = \int \psi_a^* \, H \, \psi_b \, d\tau$$

On rearranging equation (7.11) we have,

$$a_1 (H_{aa} - E \, S_{aa}) + a_2 (H_{ab} - E \, S_{ab}) = 0 \qquad (7.12)$$

On differentiating E in equation (7.6) with respect to a_2 we get,

$$a_1 (H_{ab} - E \, S_{ba}) + a_2 (H_{bb} - E \, S_{bb}) = 0 \qquad (7.13)$$

Equations (7.12) and (7.13) are known as secular equations which can be expressed in the form of determinant as follows,

$$\begin{vmatrix} H_{aa} - E \, S_{aa} & H_{ab} - E \, S_{ab} \\ H_{ba} - E \, S_{ab} & H_{bb} - E \, S_{bb} \end{vmatrix} = 0 \qquad (7.14)$$

Since the ground state atomic orbitals are identical, we have

$$H_{aa} = H_{bb}$$

$$H_{ba} = H_{ab} \qquad (7.15)$$

$$S_{ba} = S_{ab}$$

since $\int \psi_a \, H \, \psi_a^* \, d\tau = \int \psi_b \, H \, \psi_b^* \, d\tau$

$$\int \psi_a \, H \, \psi_b^* \, d\tau = \int \psi_b \, H \, \psi_a \, d\tau \qquad (7.16)$$

and $\int \psi_a \, \psi_b \, d\tau = \int \psi_b \, \psi_a \, d\tau \qquad (7.17)$

Now $S_{aa} = S_{bb}$

because $\int \psi_a^* \, \psi_a \, d\tau = \int \psi_b^* \, \psi_a \, d\tau$

Further if we use normalised wave function then $S_{aa} = S_{bb} = 1$ Consequently the secular determinant reduces to

$$\begin{vmatrix} H_{aa} - E & H_{ba} - E \, S_{ab} \\ H_{ba} - E \, S_{ab} & H_{aa} - E \end{vmatrix} = 0 \qquad (7.18)$$

which can be rewritten as,

$$(H_{aa} - E)^2 - (H_{ba} - S_{ab} \, E)^2 = 0 \qquad (7.19)$$

or

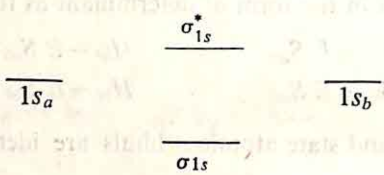
$$(H_{aa} - E) = \pm (H_{ba} - E \, S_{ab}) \qquad (7.20)$$

Solving for E, we get two values E_S and E_A, one for the symmetric energy state and the other for the antisymmetric energy state, so that

$$E_S = \frac{H_{aa} + H_{ba}}{1 + S_{ab}} \tag{7.21}$$

$$E_A = \frac{H_{aa} - H_{ba}}{1 - S_{ab}} \tag{7.22}$$

Although the original 1*s* energy state of the two hydrogen atoms are degenerate, but on combination, these split into two new energy states, one lower and the other higher in energy than the original atomic state as follows,



In terms of M.O. theory, the lower energy orbital σ_{1s} is considered to be a bonding orbital and the higher energy orbital is considered to be an antibonding orbital. Both orbitals can accomodate a pair of electrons, but the bonding orbitals, having lower energy are filled first. Thus for the hydrogen molecule ion, the electron will first occupy the bonding orbital.

7.3 Evaluation of ψ and ψ^2

On substituting the value of E in the secular equations (7.12) and (7.13) we have,

$$a_1 = a_2 \quad \text{(Symmetric solution)} \tag{7.23}$$

$$a_1 = -a_2 \quad \text{(Antisymmetric solution)} \tag{7.24}$$

Thus the two molecular orbital wave functions are,

$$\psi_S = a_1\,(\psi_a + \psi_b) \tag{7.25}$$

$$\psi_A = a_2\,(\psi_a - \psi_b) \tag{7.26}$$

It should be noted that a_1 is not known. In order to evaluate it we use the normalisation conditions:

$$\int \psi_S^2\, d\tau = 1 \tag{7.27}$$

$$\int \psi_A^2\, d\tau = 1 \tag{7.28}$$

On making proper substitutions, equation (7.27) yields,

$$\int a_1^2 \psi_a^2 \, d\tau + \int a_1^2 \psi_b^2 \, d\tau + 2a_1^2 \int \psi_a \psi_b \, d\tau = 1$$

or

$$a_1^2 + a_1^2 + 2\, a_1^2 S_{ab} = 1 \tag{7.29}$$

where normalisation condition for ψ_a and ψ_b has also been used. Equation (7.29) yields,

$$a_1 = \frac{1}{\sqrt{2 + 2\, S_{ab}}} \tag{7.30}$$

so that

$$\psi_S = \frac{1}{\sqrt{2 + 2\, S_{ab}}} (\psi_a - \psi_b) \tag{7.31}$$

On making similar substitution in equation (7.28) we get,

$$\psi_A = \frac{1}{\sqrt{2 - 2\, S_{ab}}} . (\psi_a - \psi_b) \tag{7.32}$$

The probability density ψ^2 would therefore be given by

$$\psi_S^2 = \frac{1}{2 + 2\, S_{ab}} (\psi_a^2 + \psi_b^2 + 2\, \psi_a \psi_b) \tag{7.33}$$

$$\psi_A^2 = \frac{1}{2 - 2\, S_{ab}} (\psi_a^2 + \psi_b^2 - 2\, \psi_a \psi_b) \tag{7.34}$$

If we assume $S_{ab} \ll 1$ equations (7.33) and (7.34) can be written as

$$\psi_S^2 = \tfrac{1}{2} (\psi_a^2 + \psi_b^2 + 2\, \psi_a \psi_b) \tag{7.35}$$

$$\psi_A^2 = \tfrac{1}{2} (\psi_a^2 + \psi_b^2 - 2\, \psi_a \psi_b) \tag{7.36}$$

The electron density has been plotted against the internuclear distance in Fig. 7.2(a) and 7.3 using equations (7.35) and (7.36). The corresponding plot for the individual hydrogen atoms is also given in Fig. 7.2(b). On comparing Fig. 7.2(a) and 7.2(b) we see that the symmetric function leads to an increase in electron charge density in the region of overlap between the atoms. On the other hand, the antisymmetric function leads to a decrease in charge density since from Fig. 7.3 it is obvious that the electron density is zero between the nuclei *A* and *B*.

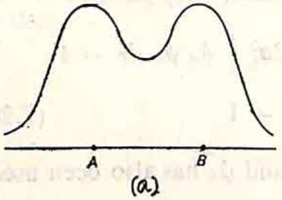


Fig. 7.2(a). Electron density as a function of distance for hydrogen molecule ion for the symmeteric state.

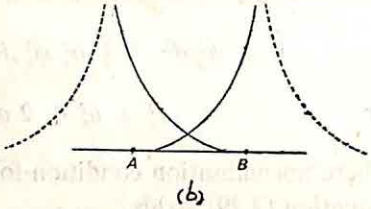


Fig. 7.2(b). Electron density as a function of distance for two separated hydrogen atoms to infinity.

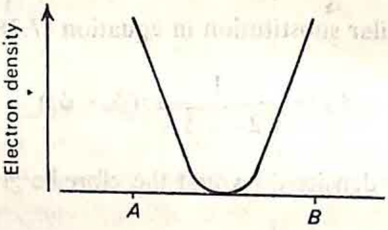


Fig. 7.3. Electron density for the antisymmetric wave function.

7.4 Comparison of Theory and Experiment

We shall now examine how far the theory developed above is in agreement with experiment. The internuclear distance and the dissociation energy for H_2^+ have been obtained from experiment. These can also be estimated from theory by plotting energy against internuclear separation. For explicit calculation of E, it is necessary to evaluate the integrals H_{aa}, S_{ba} and H_{ab}. The intergation can be done by standard methods by transforming to elliptical coordinates

Thus we have $\left(\text{in atomic units where 1 atomic unit} = \frac{4\pi^2 m e^4}{h^2}\right)$

$$H_{aa} = -\tfrac{1}{2} + \left(1 + \frac{1}{r_{12}}\right) e^{-2r_{12}} \tag{7.37}$$

$$S_{ab} = \left(\frac{r_{12}^2}{3} + r_{12} + 1\right) e^{-r_{12}} \tag{7.38}$$

$$H_{ab} = \left[\left(-\frac{1}{2} + \frac{1}{r_{12}}\right)\left(\frac{r_{12}^2}{3} + r_{12} + 1\right) - (r_{12} + 1)\right] e^{-r_{12}} \tag{7.39}$$

So that,

$$E_S = -\frac{1}{2} + \frac{1}{r_{12}} - \frac{1 + r_{12}(r_{12} + 1)\, e^{-r_{12}} - (r_{12} + 1)\, e^{-2r_{12}}}{r_{12}\left[\left(\frac{r_{12}^2}{3} + r_{12} + 1\right) e^{-r_{12}}\right]} \tag{7.40}$$

From the above equation E_S (in atomic units) can be calculated for various values of r. The results are plotted in Fig. 7.4.

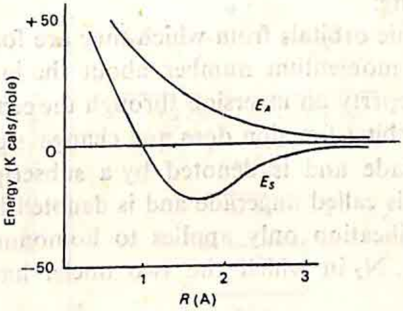


Fig. 7.4. Energy as a function of internuclear separation.

According to Fig. 7.4, the energy of antisymmetric state is never negative and hence this cannot be a stable state and thus the corresponding wave function is called antibonding orbital. On the other hand E_S is negative over a wide range of r. Further there is minimum in the curve, which corresponds to most stable state. The value of equilibrium internuclear distance r and the dissociation energy E are estimate to be 1.32 Å and 1.76 e.v. (experimental value 1.06 Å and 2.791 eV obtained from spectroscopic method). The important point about the above theory is that it gives an explanation of the stability of H_2^+ which is not possible by using thermodynamics or classical mechanics. However, it should be noted that the agreement between theory and experiment is poor.

The reason for the discrepancy is that the trial wave-function is not the true wave function. Several other trial wave-functions have been suggested which yield better agreement between theory and experiment. Two such functions are given below:

$$\psi' = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-ar_a} \tag{7.41}$$

$$\psi = e^{-c_1}(r_a + r_b)\{1 + c_2(r_a + r_b)^2\} \tag{7.42}$$

where α, a, c_1 and c_2 are constants

7.5 Excited States of H_2^+

There are other excited states of H_2^+. The molecular orbital for these states may be obtained by linear combination of hydrogen atomic orbitals for the excited states. Their nomenclature depends on the following:

1) The atomic orbitals from which they are formed.

2) Angular momentum number about the inter-nuclear axis.

3) Their property on inversion through the centre of the molecule. (If the orbital function does not change sign on inversion it is called gerade and is denoted by a subscript 'g'. If it does change sign it is called ungerade and is denoted by the subscript '*u*'. This classification only applies to homonuclear molecules such as H_2, O_2, N_2 in which the two nuclei have same atomic number.)

4) Their stability with respect to the isolated atoms. (If the energy of the orbital is lower than the energy of the corresponding isolated atoms, it is called bonding orbital. In the reverse case, it is called an anti bonding orbital.)

The M.O. nomenclature for such LCAO functions are given below:

LCOA Function	*M.O. Nomenclature*		
$1s_A + 1s_B$	$\sigma_g\, 1s$	or	$\sigma 1s$
$1s_A - 1s_B$	$\sigma_u\, 1s$	or	$\sigma^* 1s$
$2s_A + 2s_B$	$\sigma_g\, 2s$	or	$\sigma\, 2s$
$2s_A - 2s_B$	$\sigma_u\, 2s$	or	$\sigma^* 2s$

The molecular orbitals can be arranged in increasing order of energy as follows:

The energies of the molecular orbitals depend on a quantum number m similar to that for atomic orbitals. These orbitals are designated corresponding to the values of m as follows:

m	*Orbital designation*
0	σ
± 1	π
± 2	δ

m is obtained as a result of the solution of the appropriate Schrödinger equation when it is assumed that the two nuclei are stationary as justified by Born-Oppenheimer approximation. The solution is easier when elliptical coordinates are used.

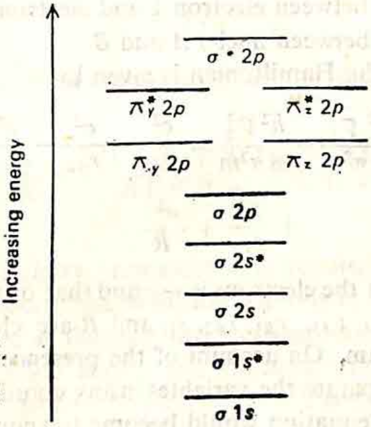


Fig. 7.5. Energy of molecular orbitals.

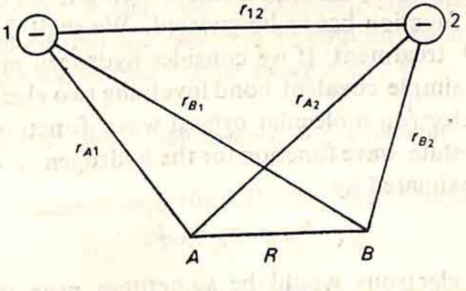


Fig. 7.6. Schematic diagram of hydrogen molecule.

7.6 Hydrogen Molecule

In the above paragraphs, we discussed the quantum mechanics of molecule containing one electron. We now proceed to study a slightly more complicated molecular system containing two electrons viz., hydrogen molecule which may be pictured as follows.

A and *B* are the two nuclei and the two electrons are denoted by 1 and 2. In writing down the expression for Hamiltonian we have to consider,

i) attraction between electron 1 and nuclei *A*.
ii) attraction between electron 2 and nuclei *B*.
iii) attraction between electron 1 and nuclei *B*.
iv) attraction between electron 2 and nuclei *A*
v) repulsion between electron 1 and eiectron 2.
vi) repulsion between nuclei *A* and *B*.

Accordingly the Hamiltonian is given by

$$H = -\frac{h^2\,\nabla_1^2}{8\,\pi^2 m} - \frac{h^2\,\nabla_2^2}{8\,\pi^2 m} - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{B2}} + \frac{r^2}{r_{12}} + \frac{e^2}{R}. \tag{7.43}$$

The charge on the electrons is $-e$ and that on the nuclei is $+e$. The distances r_{A1}, r_{A2}, r_{B1}, r_{B2}, r_{12} and R are clearly specified in the above diagram. On account of the presence of r_{12} term, it is impossible to separate the variables in any coordinate system and the Schrödinger equation would become too complicated to solve directly.

As in case of H_2^+, we will try to evaluate E, ψ and ψ^2 for the hydrogen molecule by an approximate method. As a first step a suitable trial function has to be guessed. We shall do this on the basis of *M.O.* treatment. If we consider hydrogen molecule to be formed by a simple covalent bond involving two electrons described by one electron molecular orbital wave function ψ_1 and ψ_2, then ground-state wave function for the hydrogen molecule $\psi_{M\cdot O\cdot}$ can be approximated by

$$\psi_{M\cdot O\cdot} = \psi_1\,\psi_2$$

Since the electrons would be sometimes near the hydrogen atom *A* and sometimes near the hydrogen atom *B*, we can write the electron molecular orbitals for electrons 1 and 2 using LCAO approximation as follows:

$$\psi_1 = a_1\,\psi_a^{(i)} + a_2\,\psi_b^{(i)} \tag{7.44}$$

$$\psi_2 = a_3\, \psi_a^{(2)} + a_4\, \psi_b^{(2)} \tag{7.45}$$

where $\psi_a^{(1)}$, $\psi_a^{(2)}$ are the wave functions when the electrons 1 and 2 are respectively near the nuclei A and $\psi_b^{(1)}$, $\psi_b^{(2)}$ are the corresponding wave functions when the electrons 1 and 2 are respectively near the nuclei B. Thus,

$$\psi_{M \cdot O \cdot} = [a_1\, \psi_a^{(1)} + a_2\, \psi_b^{(1)}]\, [a_3\, \psi_a^{(2)} + a_4\, \psi_b^{(2)}] \tag{7.46}$$

Using this trial wave-function and the variation method the energy (in atomic units) is found to be given by

$$E_0 = 2\, E_+ - \frac{1}{R} \tag{7.47}$$

where E_+ is the ground state energy of the hydrogen molecule ion so that

$$E_0 = -1 + \frac{1}{R} - \frac{2\,[1 + R\,(R+1)\, e^{-R} - (R+1)\, e^{-2R}]}{R\,[(R^2/3 + R + 1)\, e^{-R} + 1]} \tag{7.48}$$

Equation (7.48) neglects inter-electronic repulsion. Even if this is taken into account, the resulting E_0 versus R curve has the same general shape as that for the hydrogen-molecule ion. The calculated dissociation energy and the equilibrium inter nuclear distance are found to be 2.68 eV and 0.85 Å respectively. Experimental values 4.72 eV and 0.74 Å respectively.

In order to make further improvements in calculations, we may assume $Z_A = Z_B \neq 1$ and use Z as a parameter in the calculation just as we did in the case of variation treatment of helium atom. It is found that the energy is minimised when $Z = 1.197$, the calculated dissociation energy being 3.47 eV.

7.7 An Alternative Wave-function—V.B. Treatment

Heitler and London used the following trial function:

$$\psi_\pm = \psi_a^{(1)}\, \psi_b^{(2)} \pm \psi_a^{(2)}\, \psi_b^{(1)} \tag{7.49}$$

The wave-function can be justified on the basis of following arguments. At large internuclear separations the wave-function for the hydrogen molecule would be the product of atomic wave functions so that

$$\psi_1' = \psi_a^{(1)}\, \psi_b^{(2)} \tag{7.50}$$

and its energy would be equal to the sum of energies of atomic orbitals so that

$$E = 2\,E_4$$

In writing equation (7.50) we assume that the electron (1) is on atom *A* while the electron (2) is on atom *B*. It is also possible that the electron (2) may be on *A* and (1) may be on *B*. Accordingly the wave-function for the hydrogen molecule may also be written as follows

$$\psi_2' = \psi_a^{(2)}\,\psi_b^{(1)} \tag{7.51}$$

Since both the situations are equally probable, it is more realistic to write the wave function as suggested by equation (7.49).

Substituting appropriate values, we have

$$E_\pm = \frac{\iint [\psi_a^{(1)}\,\psi_b^{(2)} \pm \psi_a^{(2)}\,\psi_b^{(1)}]\,H.\,[\psi_a^{(1)}\,\psi_b^{(2)} \pm \psi_a^{(2)}\,\psi_b^{(1)}]\,d\tau_1\,d\tau_2}{\iint \{\psi_a^{(1)}\,\psi_b^{(2)} \pm \psi_a^{(2)}\,\psi_b^{(1)}\}^2\,d\tau_1\,d\tau_2} \tag{7.52}$$

The double integrals indicate that integration must be carried out over all space for both electrons 1 and 2. The problem is simplified by the fact that ψ_a and ψ_b are solutions of the Schrödinger equation for the two hydrogen atoms separately so that

$$\left\{-\frac{h^2\,\nabla^2}{8\,\pi^2 m}-\frac{e^2}{r_{A1}}\right\}\psi_a^{(1)} = E_H\,\psi_a^{(1)} \tag{7.53}$$

$$\left\{-\frac{h^2\,\nabla^2}{8\,\pi^2 m}-\frac{e^2}{r_{B2}}\right\}\psi_b^{(2)} = E_H\,\psi_b^{(2)} \tag{7.54}$$

Equation (7.52) can be written as

$$E_\pm = 2\,E_H - \frac{Q \pm J}{1 \pm S^2} \tag{7.55}$$

where

$$Q = \iint [\psi_a^{(1)}\,\psi_b^{(2)}]^2 \left[-\frac{e^2}{r_{B1}}-\frac{e^2}{r_{A2}}+\frac{e^2}{r_{12}}+\frac{e^2}{r_{AB}}\right] d\tau_1\,d\tau_2 \tag{7.56}$$

$$J = \iint (\psi_a^{(1)}\,\psi_b^{(1)}\,\psi_a^{(2)}\,\psi_b^{(2)}) \left[-\frac{e^2}{r_{A1}}-\frac{e^2}{r_{B2}}+\frac{e^2}{r_{12}}+\frac{e^2}{r_{AB}}\right] d\tau_1\,d\tau_2$$

and

$$S = \iint \psi_a^{(1)}\,\psi_b^{(2)}\,d\tau_1\,d\tau_2 = \iint \psi_a^{(2)}\,\psi_b^{(1)}\,d\tau_1\,d\tau_2 \tag{7.57}$$

J, Q and S are respectively called exchange, coulomb and overlap integrals. Their physical significance is as follows:

The coulomb integral Q, contains terms due to:

1) nuclear repulsion $(+\, e^2/r_{AB})$.
2) repulsion of electron cloud around nuclei A and B $(+\, e^2/r_{12})$.
3) attraction of electron cloud of electron (2) and the nuclei A $(-e^2/r_{A2})$.
4) attraction of electron cloud of electron (1) and the nuclei B $(-e^2/r_{B1})$

The exchange integral J includes terms

a) due to repulsion between electron clouds of electrons (1) and (2).
b) due to attraction between electron cloud of electron (1) and the nucleus A.
c) due to attraction between the electron cloud of electron (2) and the nucleus.
d) due to repulsion between the nuclei and A and B.

The overlap integral S measures the extent to which the atomic orbitals described by ψ_a and ψ_b reinforce or overlap each other.

The coulomb exchange and overlap integrals can be calculated by standard methods. Thus, values for $E_\pm$ for various internuclear distances can be obtained. These are plotted in Fig. 7.7. E_H denotes the energy of hydrogen atom.

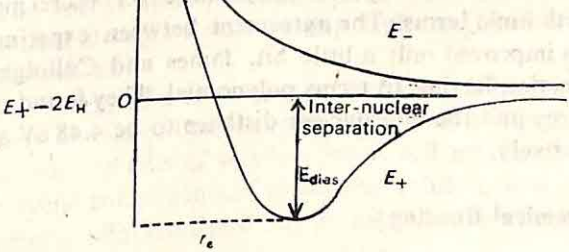


Fig. 7.7. Energy for the hydrogen molecule.

The co-ordinates of minimum in the above curve yield the value of dissociation energy (E_{diss}) and equilibrium inter-nuclear distance (r_e). These are found to be 3.14 eV and .87 Å.

7.8 Comparison of V.B. and M.O. Wave-functions

Expanding $\psi_{M \cdot O}$. as given by equation (7.46) we have,

$$\psi_{M \cdot O} = a_1 a_3 \psi_a^{(1)} \psi_a^{(2)} + a_2 a_4 \psi_b^{(1)} \psi_b^{(2)} + [a_1 a_4 \psi_a^{(1)} \psi_b^{(2)} + a_2 a_3 \psi_b^{(1)} \psi_a^{(2)}] \quad (7.58)$$

whereas $\psi_{V \cdot B} = \psi_a^{(1)} \cdot \psi_b^{(2)} \pm \psi_a^{(2)} \psi_b^{(1)}$ as given by equation (7.49). It is obvious that $\psi_{V \cdot B}$ and $\psi_{M \cdot O}$. are similar except an extra term which is within bracket in equation (7.58). This extra term is due to the coming of the electrons near a particular nuclei. In other words, $\psi_{M \cdot O}$. gives a large weight to configuration that places both electrons on one nucleus, which correspond to ionic structures $A^+ B^-$ and $A^- B^+$. The *V.B.* wave-function ignores these ionic terms. It essentially attempts to estimate the interaction which results as the two separate atoms are brought together.

V.B. wave-function is more susceptible to refinement in contrast to the *M.O.* wave-function, hence the former is often capable of greater accuracy. However considerable amount of labour is involved in following *V.B.* method. On the other hand *M.O.* wave-function is simple and yields conclusions of great chemical interest in a simple manner.

7.9 Further Refinements

The wave functions described above can be improved by the inclusion of more terms involving screening effect or screening effect along with ionic terms. The agreement between experiment and theory is improved only a little bit. James and Collidge used a wave-function having 13-terms polynomial. They found dissociation energy and the internuclear distance to be 4.48 eV and 0.74 Å respectively.

7.10 Chemical Bonding

Binding in molecules is essentially based on the following principles:

i) Two electrons with different spin tend to come together.

ii) Two electrons with the same spin tend to keep apart.

When two hydrogen atoms come together, the two electrons will tend to move into the internuclear region due to electrostatic attraction exerted by the nuclei. If the two electrons have the same spin, both spin and charge correlation will tend to keep them apart and so the probability of both the electrons being simultaneously between the nuclei will be small and there will be no resultant inter-atomic attraction. On the other hand, if the electrons are of opposite spin, then spin correlation, tending to bring the electrons together, will overcome to some extent their mutual repulsion and both electrons may be in the internuclear region, leading to an inter-atomic force of attraction, or cohesive force known as the covalent bond.

The molecular system is conveniently described in terms of molecular orbitals, which are formally analogous to the atomic orbitals. Molecular orbitals for an n-atom molecule are assumed to possess the following properties:

a) Each electron in the molecule is described by a wave-function ϕ. These wave-functions are called molecular orbitals. These are polycentric so that the electron moves in the field of all n nuclei.

b) Each molecular orbital has its own energy.

c) The molecular orbital consists of a series of super-imposed self-consistent atomic orbitals i.e.

$$\phi = \sum_{r=1}^{n} c_r \psi_r$$

where C's are coefficients.

d) The energy of a molecular orbital is least, when the component atomic orbitals overlap with one another as much as possible.

e) The energy of a molecular orbital is least when the component atomic orbitals have equal or nearly equal energies. Atomic orbitals of very low energy will not therefore readily become components of molecular orbitals, and hence the inner orbital electrons may be neglected for bonding purposes since these are non-bonding.

f) Each electron has a specific spin governed by the Pauli Principle. This in effect means that the total wave-function $\psi = \phi\ (n, l, m, s)$ must be antisymmetric. This is explained below.

7.11 Spin Pairing and Chemical Bond

In quantum mechanics, all the wave-functions are not acceptable. The acceptable wave-function must either be symmetric or antisymmetric with respect to interchange of the co-ordinates of the particles depending on their nature.

If follows from the relativistic quantum field theory* that all particles with half integral spin belong to antisymmetric class and those with 0 or integral spin to symmetric class. Thus for electrons, any acceptable wave function must be antisymmetric with respect to the interchange of electrons or in other words the sign of wave function must change when the electrons are exchanged (Pauli principle). This principle applies to electrons in both molecular and atomic orbitals.

For a system of n electrons, the polyelectronic wave-function is conveniently expressed in the form of a determinant, since interchanging rows or columns of a determinant changes the algebraic sign,

$$\psi_{(1,2,3\ldots n)} = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_a(1) & u_b(1) & \ldots & u_n(1) \\ u_a(2) & u_b(2) & \ldots & u_n(2) \\ u_a(3) & u_b(3) & \ldots & u_n(3) \\ \ldots & \ldots & & \ldots \\ \ldots & \ldots & & \ldots \\ u_a(n) & u_b(n) & & u_n(n) \end{vmatrix}$$

where ψ $(1, 2, \ldots, n)$ is polyelectronic wave-function and $u_a, u_b \ldots$ etc. are different single particle wave-functions or orbitals. The states $a, b, \ldots, n$ are characterised by particular set of four quantum numbers namely n, l, m, and s. The factor $\sqrt{n!}$ is the normalising factor and arises because there are ways of assigning electrons 1, 2, etc. to states or orbitals $a, b, c, \ldots$ etc. Since $\psi(1, 2, \ldots, n) \neq 0$, no two columns or no two rows can be alike, otherwise the determinant would be zero. Hence, it follows that no two atomic electrons can have the same four quantum numbers.

---

*Merzbacher, E., *Quantum Mechanics*, John Wiley and Sons Inc., p. 426.

7.11.1 SPIN PAIRING AND COVALENT BOND

Let us consider a system of two electrons. The non-spin part of the wave-function for hydrogen is written as

$$\psi_+ = u_a(1)\, u_b(2) + u_a(2)\, u_b(1) \tag{1}$$

ψ_+ is symmetric wave-function, since if we interchange electrons 1 and 2 the wave-function remains unchanged. The other possible wave-function is given by:

$$\psi_- = u_a(1)\, u_b(2) - u_a(2)\, u_b(1) \tag{2}$$

ψ_- is antisymmetric, since it would change sign if we interchange the electrons.

Further, it can be noted that the total wave-function is a product wave-function of the space wave-function $\psi_\pm$ and spin wave-function ψ_{spin} i.e.

$$\psi_{total} = \psi_\pm \times \psi_{spin}$$

we can introduce electron spin by terms α (if $s = \frac{1}{2}$) or β (if $s = -\frac{1}{2}$). So that for two electron system, in which both electrons have parallel spins, we may write

$\psi_{1spin} = \alpha(1)\,\alpha(2)$ ↑ ↑ Spin parallel in upward direction
$\psi_{2spin} = \beta(1)\,\beta(2)$ ↓ ↓ Spin parallel in downward direction.

If two electrons have opposite spin, the interchange of electrons lead to two further functions:

$\psi_{3\,spin} = \alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)$ resultant spins parallel
$\psi_{4\,spin} = \alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)$ resultant spins paired

which arises in exactly the same way as the two space functions $\psi_\pm$. Thus,

ψ_1 spin is symmetric,
ψ_2 spin is symmetric,
ψ_3 spin is symmetric, and
ψ_4 spin is antisymmetric.

A stable hydrogen molecule has singlet ground state and is described by the wave function.

$$\psi_{\text{total}} = \psi_+ \times \psi_{4\,\text{spin}}$$
$$= (u_a(1)\, u_b(2) + u_a(2)\, u_b(1))\,(\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1))$$

The repulsive state of the hydrogen molecule is described by the total wave function:

$$\psi^{-}{}_{\text{total}} = (u_a\,(1)\;u_b\,(2) - u_a\,(2)\;u_b\,(1)) \begin{cases} \alpha\,(1)\;\alpha\,(2) \\ \beta\,(1)\;\beta\,(2) \\ \alpha\,(1)\;\beta\,(2) + \alpha\,(2)\;\beta\,(1) \end{cases}$$

There are three symmetric wave-function hence the repulsive state or excited state of hydrogen molecule would be a triplet state.

Thus if follows that it is a consequence of exclusion principle that spin pairing is essential for covalent bond formation. For the simplest case of H_2 as discussed above, the normal hydrogen atoms attract each other only when the spin of two electrons are antiparallel or paired, whereas, they repel each other when the spins are parallel.

7.12 Energy of Molecular Orbitals

Just as there is an order of filling of atomic orbitals, there is an order of filling of molecular orbitals the lower energy orbital being filled first. The energies are in the following order*,

$$\sigma 1s < \sigma^{*}1s < \sigma 2s < \sigma^{*}2s < \sigma 2p < \pi_y\,2p = \pi_z\,2p < \pi^{*}_y\,2p$$
$$= \pi^{*}_z\,2p < \sigma^{*}\,2p$$

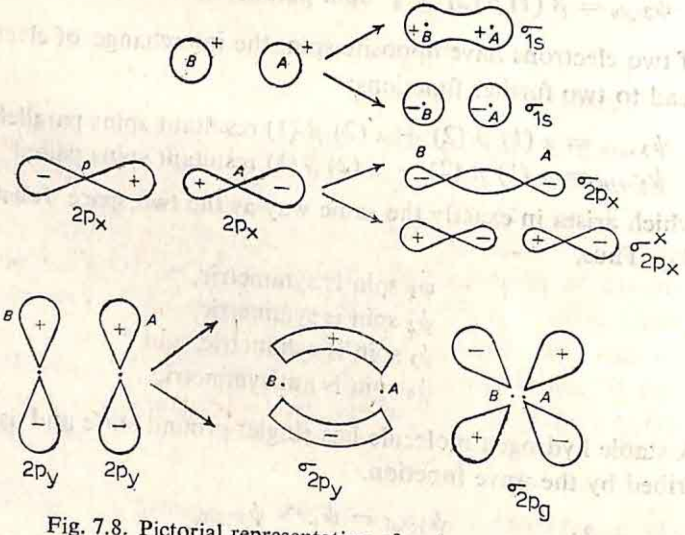


Fig. 7.8. Pictorial representation of molecular orbitals formed from atomic orbitals.

In the case of homonuclear diatomic molecule we can give a simple pictorial representation of the angular variation of molecular orbitals when they are formed from linear combination of individuals atomic orbitals is given in Fig. 7.8.

The molecular orbitals formed from 1*s* atomic orbitals have cylindrical symmetry about the internuclear axis. Such bonds are referred to as σ-bonds. Combination of two p_z and p_y orbitals show a quite different symmetry with respect to bond axis. These bonds are called π-bonds and since they can be formed from either p_z or p_y atomic orbitals, they are designated as π_z and π_y respectively.

Examples of other types of overlap between various orbitals are given in Fig. 7.9.

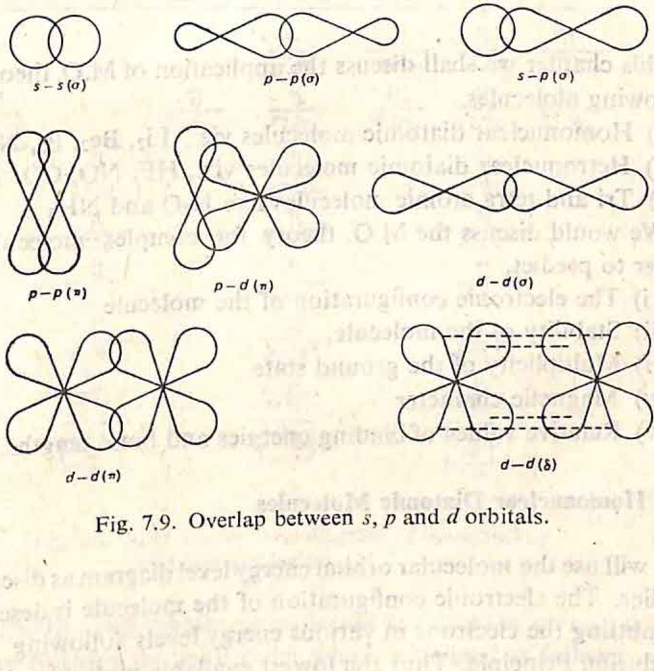


Fig. 7.9. Overlap between *s*, *p* and *d* orbitals.

CHAPTER 8

Small Inorganic Molecules

In this chapter we shall discuss the application of M.O. theory to following molecules.

a) Homonuclear diatomic molecules viz., Li_2, Be_2, B_2, N_2, O_2
b) Hetronuclear diatomic molecules viz., HF, NO, CO, LiH
c) Tri and tetra atomic molecules like H_2O and NH_3

We would discuss the M.O. theory for complex molecules in order to predict,

i) The electronic configuration of the molecule
ii) Stability of the molecule.
iii) Multiplicity of the ground state.
iv) Magnetic character
v) Relative values of binding energies and bond lengths.

8.1 Homonuclear Diatomic Molecules

We will use the molecular orbital energy level diagram as discussed earlier. The electronic configuration of the molecule is described by putting the electrons in various energy levels following Pauli Exclusion Principle. Thus the lowest available molecular orbital energy level would be first occupied by a pair of electrons. We give the M.O. description of a few diatomic molecules.

The M.O. energy level diagrams for typical molecules are given in Fig. 8.1.

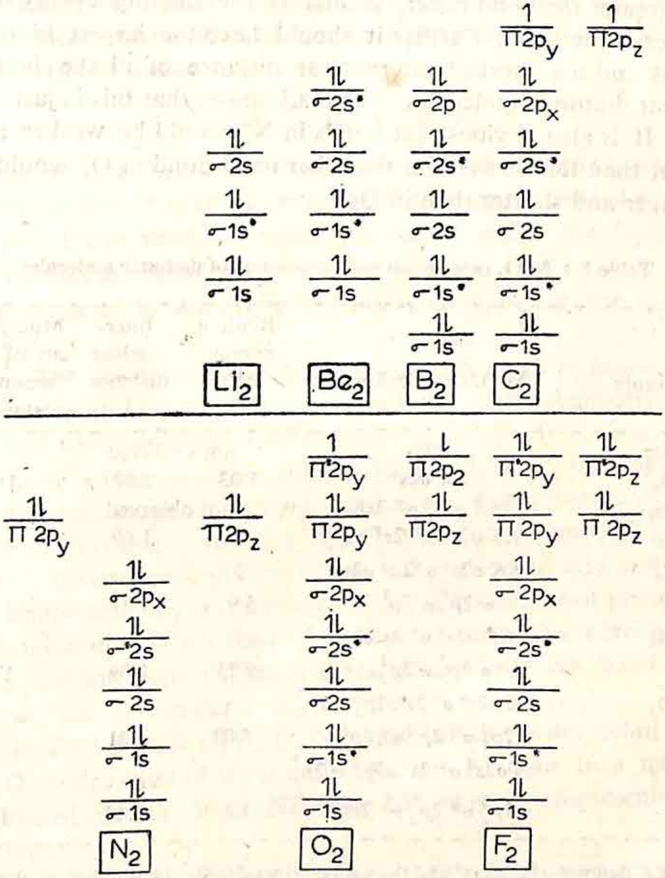


Fig. 8.1. M.O. energy level diagram of homonuclear inorganic molecules.

In order to guess whether a molecule would exist or not, it is necessary to calculate bond order which is defined as follows:

$$\text{Bond order} = \frac{\text{No. of bonding electrons} - \text{No. of antibonding electrons}}{2}$$

A molecule would be non-existent if the bond order is zero.

Using this criterion it is obvious that all the above diatomic molecules would be stable except He_2 and Be_2. It is also obvious that greater the bond order, greater is the binding energy and shorter is the bond. Further it should have the largest binding energy and the shortest internuclear distance of all the homonuclear diatomic molecules. Table 8.1 shows that this is just the case. It is also obvious that bonds in N_2^+ would be weaker and longer than that in N_2. On the other hand bond in O_2^+ would be stronger and shorter than in O_2.

Table 8.1 M.O. description and parameters of diatomic molecules

Molecule	M.O. description	Binding energy (eV)	Inter-nuclear distance Å	Multiplicity of the ground state
He_2	KK	not observed		
Li_2	$KK\ \sigma 2s^2$	1.03	2.67	1
Be_2	$KK\ \sigma 2s^2\ \sigma^* 2s^2$	not observed		
B_2	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2$	3.0	1.59	3
C_2	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2\ \pi 2p_y^1\ \pi 2p_z^1$	5.9	1.31	1
N_2	$KK\ \sigma 2s^2\ \sigma^* 2s^2 \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2$	9.756	1.09	1
O_2	$KK\ \sigma 2s^2\ \sigma^* 2s^2 \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^* 2p_z^1\ \pi^* 2p_y^1$	5.08	1.21	
F_2	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^* 2p_z^2\ \pi^* 2p_y^2$	1.6	1.44	1

KK denotes $\sigma 1s^2\ \sigma^* 1s^2$ and the superscripts denote the number of electrons in the particular energy state.

Molecular orbital energy level diagram also gives an insight into the nature of bonds. Thus it easily follows that in N_2, out of the three effective bonds, one is a σ-bond and the other two are π-bonds. We can also find out the number of unpaired electrons in the molecule, which determines the magnetic character of the molecules. Thus, N_2 should be diamagnetic whereas O_2 and N_2^+ would be paramagnetic.

8.2 Heteronuclear Diatomic Molecules

Even for heteronuclear diatomic molecules AB, the molecular orbital in the region of each atom will resemble an atomic orbital on that atom. Hence we assume that the molecular orbital will be a linear combination of atomic orbitals (L.C.A.O.) which we may write as follows

$$\psi = C_A \, \psi_A + C_B \, \psi_B \tag{8.1}$$

where ψ_A and ψ_B are the atomic orbitals and C_A and C_B are constants so chosen that the energy of the molecular orbital in minimum. Little or no combination occurs unless the following conditions are satisfied.

i) ψ_A and ψ_B are orbitals of similar energies for the isolated atoms,

ii) The atomic orbitals should overlap as much as possible,

iii) the atomic orbitals must have the same symmetry with respect to internuclear axis *A-B*.

For a homonuclear diatomic molecule $C_A = C_B$ but this is not so for hetronuclear diatomic molecules. The polarity of such molecules is due to the fact that C_A and C_B are unequal and if C_A^2/C_B^2 is very much different from unity, the molecule will have an appreciable dipole moment. C_A^2/C_B^2 is a measure of polarity of this molecule. When the ratio is exactly unity, this corresponds to a covalent bond. When it is less than unity, the bond has a certain ionic character also.

We shall discuss HF, CO, NO, and LiF in greater detail. The M.O. designation of these molecules can be done in a manner discussed earlier. Thus HF and NO may be represented as follows:

$$\text{H}\,(1s) + \text{F}\,(1s^2\,2s^2\,2p^5) \rightarrow \text{HF}\,[\sigma\,1s^2\;\sigma\,2s^2\;\sigma\,2p_x^2\;\pi\,2p_y^2\;\pi\,2p_z^2]$$

$$\text{N}\,(1s^2\,2s^2\,2p^3) + \text{O}\,(1s^2\,2s^2\,2p^4) \rightarrow \text{NO}\,[KK\,\sigma\,2s^2\;\sigma^*\,2s^2\;\sigma\,2p_x^2\;\pi\,2p_y^2\;\pi\,2p_z^2\;\pi^*\,2p_y^1]$$

The molecular orbitals ψ_σ and ψ_{σ^*} for HF, using equation (8.1) can be written as:

$$\psi_\sigma = N\,[1s\,(\text{H}) + \lambda_1\,2p\,(\text{F})] \tag{8.2}$$

and

$$\psi_\sigma = N\,[1s\,(\text{H}) - \lambda_2\,2p\,(\text{F})] \tag{8.3}$$

where N is the normalisation constant, λ_1 and λ_2 are constants. $\lambda_2 < 1$ but $\lambda_1 > 1$. The M.O. diagram may be represented as in Fig. 8.2.

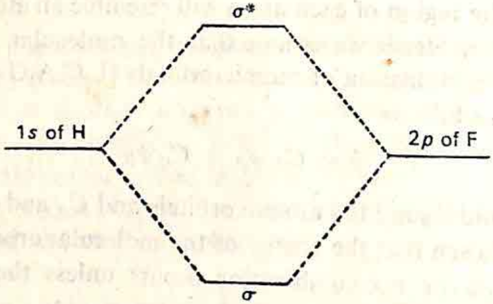


Fig. 8.2. M.O. diagram of HF.

It should be noted that the $1s^2$ and $2s^2$ orbitals of fluorine have energy much lower than of Hydrogen $1s$ orbital. The bonding molecular orbital results from the overlap of a $2p$ orbital of fluorine and $1s$ orbital of hydrogen. The bonding M.O. is polarised so that the larger fraction of bonding electron density is near the fluorine atom. The calculation shows that HF bond distance is 0.92×10^{-8} cm, whereas this charge on hydrogen atom and fluorine atom is $+0.43$ and -0.43 respectively.

$$\overset{+0.43}{\mathrm{H}} \underset{0.92 \times 10^{-8}\ \mathrm{cm}}{\underline{\qquad\qquad\qquad}} \overset{-0.43}{\mathrm{F}}$$

Molecular orbital wave function for CO can be written as follows:

$$\psi_\pi = 0.47\ [2p\ (\mathrm{C})] + 0.77\ [2p\ (\mathrm{O})] \tag{8.4}$$

since $2p$ orbitals of carbon as well as oxygen have similar energy. N_2 and CO are isoelectronic. Further, for N_2, we have

$$\psi_\pi = 0.62\ [2p\ (\mathrm{N})_A + 2p\ (\mathrm{N})_B] \tag{8.5}$$

where A and B refer to the two atoms of nitrogen.
In LiH, molecule, overlap between $2s$ and $2p$ orbitals of Lithium and $1s$ orbitals of hydrogen is possible. Accordingly we have,

$$\psi_{LiH} = 0.700\ [1s\ (\mathrm{H})] + 0.328\ [2s\ (\mathrm{Li})] + 0.204\ [2p\ (\mathrm{Li})] \tag{8.6}$$

8.3 Polyatomic Inorganic Molecules

One of the more outstanding success of the quantum mechanical approach to molecules has been in the prediction of molecular geometry. In terms of valence bond theory, a covalent bond is imagined to be formed as the result of pairing of the two electrons in atomic orbitals of two different atoms. The bond is supposed to lie along the direction in which the orbitals overlap. The strongest bond would be formed in the position which permits the maximum possible overlap between the two orbitals.

The concept of electron pair bond has been widely used in modern chemistry. Such bonds are assumed to retain their identity regardless of what the rest of the molecule excluding the bond is like. Such an assumption is justified by (i) the prediction of thermodynamic properties based on bond energies and (ii) the use of bond frequencies in *IR* spectroscopy for identification of unknown compounds. In quantum mechanics also, bond eigenfunctions are widely used. We will discuss the use of bond eigenfunction in relation to water molecule.

Oxygen atom in the ground state has the electronic configuration

$$1s^2\, 2s^2\, 2p^4 \text{ or } \quad \overset{1s}{\boxed{\downarrow \mid \uparrow}} \quad \overset{2s}{\boxed{\uparrow \mid \downarrow}} \quad \overset{2p}{\boxed{\uparrow\downarrow \mid \uparrow \mid \uparrow}}$$

where we have two unpaired electrons. These two electrons can be used to form bonds with other atoms. The wave function for the water molecule can be thought of as a product of two bond eigenfunction so that

$$\psi_{\mathrm{H_2O}} = \psi_{\mathrm{OH}} \cdot \psi_{\mathrm{OH}}$$

where

$$\psi_{\mathrm{OH}} = \mathrm{N}\,[\psi_{2p}\,(\mathrm{O}) \cdot \psi_{1s}\,(\mathrm{H}) + \psi_{2p}\,(\mathrm{H})\, \psi_{1s}\,(\mathrm{O})]$$

where (O) represents this electron associated with oxygen nuclei and (H) represents this electron associated with hydrogen nuclei and where there is a possibility of interchange. In order to obtain a maximum possible overlap between 1*s* orbitals of the hydrogen atoms and the $2p_x$ and $2p_y$ orbitals of the oxygen atom, it is necessary for the electrons of H orbitals and that of oxygen orbitals to overlap along *x* and *y*-axis. This is shown in Fig. 8.3, which indicates that ∠HOH should be 90°.

The experimental value, however, is 104.31°. According to this model, the binding energy of the water molecule should be twice the energy of an OH-bond. This is approximately correct. The above treatment was refined by Ellision and Shull (1953-55) who used self-consistent field orbitals instead of atomic orbitals. The

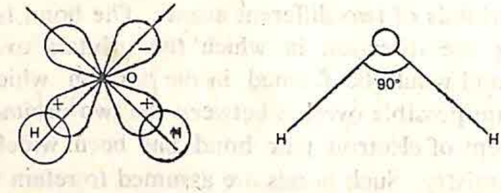


Fig. 8.3. Schematic representation of overlap in water molecules.

calculated values of bond angle and dipole moment of water molecule were found to be 105° and 1.52 D respectively. The latter is in poor agreement with the experimental value (1.83 D). Further refinements were made by Duncan and Pope using hybrid orbitals.

The valence bond approach can be applied to triatomic molecules of similar nature such as H_2S, H_2Se and H_2Te. Further, the method can be applied to other complex molecules like NH_3, PH_3, AsH_3 and SbH_3. We will examine the case of NH_3 as a typical case, where the 1*s* orbitals of the hydrogen atoms overlap with the *p*-orbitals of N atom, we note that N has the following configuration,

$$1s^2\, 2s^2\, 2p_x^1\, 2p_y^1\, 2p_z^1$$

The molecular wave function would be the product of three NH bond eigenfunctions, so that

$$\psi_{NH_3} = \psi_{NH} \cdot \psi_{NH} \cdot \psi_{NH}$$

where $\psi_{NH} = N\,\{\psi_{2p}(N)\,\psi_{1s}(H) + \psi_{2p}(H)\,\psi_{1s}(N)\}$

In order to obtain maximum overlap the 1*s* orbitals of hydrogen must overlap *p* orbitals of nitrogen along *x*, *y* and *z*-axis. This would lead to overlap in the following manner with a bond $\angle$HNH equal to 90° as shown in Fig. 8.4.

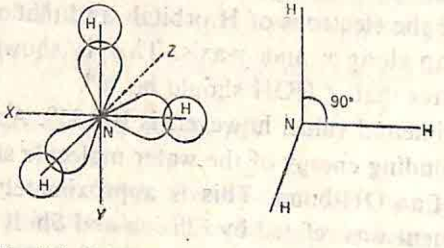


Fig. 8.4. Schematic representation of overlap in ammonia molecule.

8.4 Hybrid Orbitals

We have seen that ψ_{1s}, ψ_{2p}, ψ_{2s} are acceptable solutions of the appropriate Schrödinger equation for hydrogen like atoms. In order to explain bonding in certain compounds such as $BeCl_2$, BCl_3 and CCl_3 it is necessary to look for the other possible solutions of Schrödinger equation. It is known that combination of solutions of a differential equation are also a solution of the differential equation. The best way to guess alternative solutions is to start with a combination of these orbitals as solutions. In this fashion two or more orbitals can be combined to yield a hybrid orbital. We shall examine the new wave functions obtained by combining two orbitals.

a) COMBINATION OF 1*s* AND ONE 2*p* ORBITAL

The new wave functions for the two electrons involved for such a case are given by

$$\psi_1 = C_{11}\,\psi s + C_{12}\,\psi_p \qquad (8.7)$$

$$\psi_2 = C_{21}\,\psi s + C_{22}\,\psi_p \qquad (8.8)$$

The coefficients can be evaluated by applying normalisation and orthogonality theorem. Thus,

$$\int \psi_1^2\, d\tau = \int C_{11}^2\, \psi_s^2\, d\tau + 2\, C_{11}\, C_{12} \int \psi_s\, \psi_p\, d\tau + \int C_{12}^2\, \psi_p^2\, d\tau = 1$$

Further since,

$$\int \psi_s^2\, d\tau = 1; \int \psi_p^2\, d\tau = 1 \text{ and } \int \psi_s\, \psi_p\, d\tau = 0$$

we have

$$C_{11}^2 + C_{12}^2 = 1 \qquad (8.9)$$

Similarly, using normalisation condition for ψ_2, we would get

$$C_{12}^2 + C_{22}^2 = 1 \qquad (8.10)$$

Further since $\int \psi_1\, \psi_2\, d\tau = 0$, we have

$$C_{11}\, C_{21} + C_{12}\, C_{22} = 0 \qquad (8.11)$$

Equations (8.9), (8.10) and (8.11) taken together yield,

$$|C_{11}| = +|C_{12}| = |C_{21}| = -|C_{22}| = \frac{1}{\sqrt{2}} \qquad (8.12)$$

From the view-point of directional bonding, we are only interested in angular dependent part, and for this purpose we simply write

$$\psi_s = \frac{1}{\sqrt{4\pi}} \tag{8.13}$$

$$\psi_{2p} = \frac{\sqrt{3}}{\sqrt{4\pi}} \cos\phi \tag{8.14}$$

where the radial part has been ignored. Thus,

$$\psi_1 = \frac{1}{\sqrt{2}}\psi_s + \frac{1}{\sqrt{2}}\psi_p$$

$$= \frac{1}{\sqrt{4\pi}}\cdot\frac{1}{\sqrt{2}}(1+\sqrt{3}\cos\phi)$$

and

$$\psi_2 = \frac{1}{\sqrt{2}}\psi_s - \frac{1}{\sqrt{2}}\psi_p = \frac{1}{\sqrt{4\pi}}\cdot\frac{1}{\sqrt{2}}$$

$$(1-\sqrt{3}\cos\phi) \tag{8.15}$$

We can plot the angular dependence of the *sp* hybrid wave function as we did in the case of *s* and *p* orbitals for hydrogen atom. This is shown in Fig. 8.5 which is obtained by plotting ψ for various values of ϕ

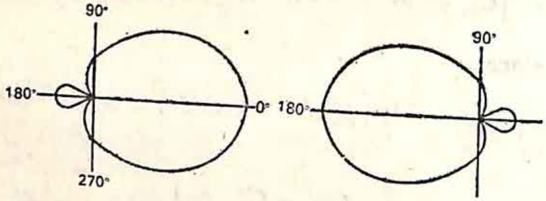


Fig. 8.5. Angular variation of *sp* hybrid orbitals.

sp hybrid orbitals can explain why Be and Hg are divalent. Using these we can show that $BeCl_2$ and $HgCl_2$ would be linear as is actually found to be the case. The orbital diagram for the latter may be expressed as shown in Fig. 8.6.

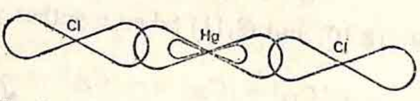


Fig. 8.6. Orbital picture of bending in $HgCl_2$.

b) COMBINATION OF $2s$ AND TWO $2p$ ORBITALS

Since in this case wave-functions for three electrons are combined, the appropriate hydrid wave-function can be written as

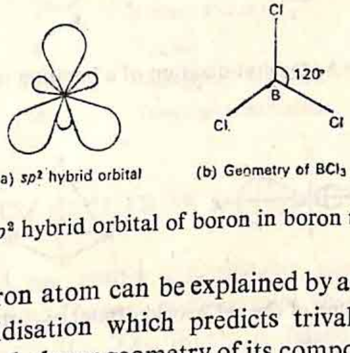
$$(\psi_{sp^2})_1 = \frac{1}{\sqrt{3}}\,\psi_{2s} + \sqrt{\frac{2}{3}\,\psi_{2p_x}} \tag{8.16}$$

$$(\psi_{sp^2})_2 = \frac{1}{\sqrt{3}}\,\psi_{2s} - \frac{1}{\sqrt{6}}\,\psi_{2p_x} - \frac{1}{\sqrt{2}}\,\psi_{2p_y} \tag{8.17}$$

$$(\psi_{sp^2})_3 = \frac{1}{\sqrt{3}}\,\psi_{2s} - \frac{1}{\sqrt{6}}\,\psi_{2p_x} + \frac{1}{\sqrt{2}}\,\psi_{2p_y} \tag{8.18}$$

where the constants are determined in the usual manner.

The wave functions or the electron density for the three orbitals can be plotted against this angle ϕ as was done for the case of sp hybrid orbital. Each orbital yields a lobe making an angle of 120° with the lobe due to other orbital. Thus angular variation of sp^2 hybrid orbitals is depicted as follows (Fig. 8.7).



(a) sp^2 hybrid orbital (b) Geometry of BCl_3

Fig. 8.7. sp^2 hybrid orbital of boron in boron trichloride.

Bonding with boron atom can be explained by assuming the existence of sp^2 hybridisation which predicts trivalent character of Boron and trigonal planar geometry of its compounds. Thus orbital diagram of BF_3 would be represented as shown in Fig. 8.8.

c) COMBINATION OF ONE $2s$ AND THREE $2p$ ORBITALS

Four hybrid orbitals t_1, t_2, t_3, t_4 are formed by such a combination. These are

$$\psi_{t_i} = \frac{1}{2}\,\psi_{2s} + \frac{\sqrt{3}}{2}\,\psi_{2p_x} \tag{8.19}$$

$$\psi_{t_2} = \frac{1}{2}\,\psi_{2s} - \frac{1}{2\sqrt{3}}\,\psi_{2p_x} + \frac{\sqrt{2}}{3}\,\psi_{2p_z} \tag{8.20}$$

$$\psi_{t_3} = \frac{1}{2}\,\psi_{2s} - \frac{1}{2\sqrt{3}}\,\psi_{2p_x} + \frac{1}{\sqrt{2}}\,\psi_{2p_y} - \frac{1}{\sqrt{6}}\,\psi_{2p_z} \qquad (8.21)$$

$$\psi_{t_4} = \frac{1}{2}\,\psi_{2s} - \frac{1}{2\sqrt{3}}\,\psi_{2p_x} - \frac{1}{\sqrt{2}}\,\psi_{2p_y} - \frac{1}{\sqrt{6}}\,\psi_{2p_z} \qquad (8.22)$$

Angular variation of a single tetrahedral orbital would be represented as

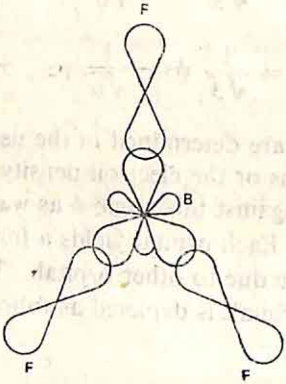


Fig. 8.8. Orbital diagram of a bonding in BF_3.

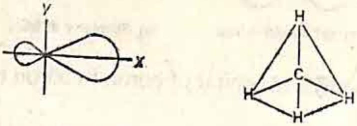


Fig. 8.9. One of the sp^3 hybrid orbital of carbon in CH_4.

The four orbitals are spatially directed towards the corners of a regular tetrahedron as shown above. These orbitals combine with 1*s* orbitals of hydrogen to form a set of localised molecular orbitals for methane (Fig. 8.9). Thus methane is a tetrahedral molecule with hydrogen atoms occupying the corners of a tetrahedron and carbon sitting at the centre. This type of hybridisation is called sp^3 hybridisation.

We can also have combination of *d* orbitals with *s* and *p* orbitals in the above manner to yield corresponding hybrid orbitals. The shapes of molecules and the type of hybridisation are given in Table 8.2 for a few molecules.

Table 8.2 Hybridisation and shapes of molecules

Hybridisation	No. of bonding pairs	Shapes of molecules	Example
sp	2	Linear	$HgCl_2$
sp^2	3	Planar triangle	BF_3
sp^2	2	V-shaped (120°)	$SnCl_2$
sp^3	4	Tetrahedron	CH_4
,,	3	Trigonal pyramid	NH_3
,,	2	V-shaped (109.5°)	OH_2
,,	1	Linear	FH
sp^3d	5	Trigonal bipyramid	PCl_5 (gas)
,,	4	Irregular tetrahedron	SCl_4
,,	3	T-shape	ClF_3
,,	2	Linear	ICl_2
$sp^3\ d^2$	6	Octahedron	SF_6, PF_6
,,	5	Square pyramid	IF_5
,,	4	Square	ICl_4
$sp^3\ d^3$	7	Pentagonal bipyramid	IF_7
,,	4	Irregular octahedron	$SbBr_6$

APPENDIX: ELECTRON REPULSION THEORY

A theory based on purely electrostatic considerations called 'Electron Repulsion Theory' is sometimes very useful in predicting molecular geometry. The theory is based on the fact that electrons tend to avoid each other as much as possible. There are two reasons for it:

i) There is a strong force of repulsion between electrons.

ii) Any two electrons with the same spin tend to avoid each other since such electrons would have almost zero probability of being in the same region of space. The molecular geometry would, therefore, be essentially influenced by the number of electron pairs according to the following table.

The magnitude of bond angle may differ from case to case since

lone-pair-lone pair repulsion < lone pair-bond pair repulsion < bond pair-bond pair repulsion.

The above concept is useful in explaining the molecular geometry. Table 8.3 shows how the number of electron pairs influence the molecular geometry.

Table 8.3 Molecular geometry and electron pairs

No. of electron pairs	Molecular geometry
Two	Linear
Three	Trigonal
Four	Tetrahedron
Five	Trigonal bipyramid
Six	Octahedron
Seven	Pentagonal bipyramid

CHAPTER 9

Symmetry of Molecules and Orbitals

Molecular orbital treatment is fairly simple for small molecules. However, it becomes complicated when we deal with complex polyatomic molecules. For example in SF_6, we have to take into account the bonding between one 2*s*, three 2*p* orbitals for each fluorine atom and one 3*s* three 3*p* orbitals of sulphur atom so that 28 orbitals would be involved in the problem. In order to determine the energies of each of the 28 resulting M.O.'s and $28 \times 28 = 784$ coefficients one has to solve 28×28 determinant. This is humanly not possible and only high speed computors are capable of accomplishing it.

In order to simplify the M.O. treatment, symmetry consideration are used as a first step since we know that only orbitals having similar symmetry can be combined by L.C.A.O. to yield M.O.'s. This is not easy to do by simple inspection. For this purpose, symmetry consideration coupled with concepts of group theory are employed. We shall first discuss the former.

9.1 Symmetry of Molecules

A molecule may possess several elements of symmetry which may include.

i) axes of symmetry,
ii) planes of symmetry, and
iii) an 'inversion centre' or centre of symmetry.

9.1.1 AXIS OF SYMMETRY

It may be defined as an axis around which rotation of the molecule by a certain angle produces an equivalent configuration of the molecule. The axis of symmetry for the water molecule lies in the molecular plane and bisects the angle HOH (Fig. 9.1) since the symmetry operation of rotation by 180° about the axis leads to interchange of the two hydrogen atoms. The configuration of the molecule remains unchanged.

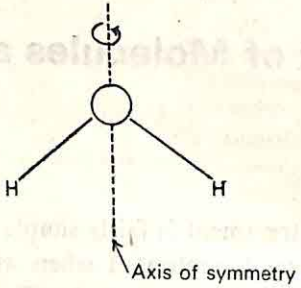


Fig. 9.1. Axis of symmetry for water molecule.

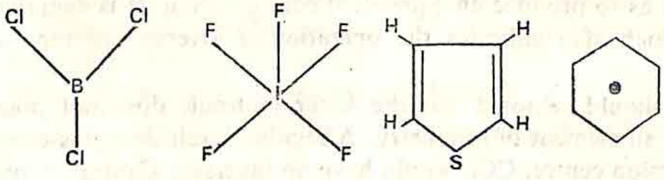
We characterise the symmetry axis by its order which is defined as follows:

$$\text{order of symmetry axis} = \frac{360}{\theta}$$

where θ is the number of degrees through which it is necessary to rotate the molecule to produce an equivalent configuration. Thus for water molecule the order of symmetry axis is $\frac{360}{180} = 2$ and the symmetry axis is represented by C_2 where C represents the symmetry operation and the subscript 2 represents the order. In the same manner, H_2S would have C_2 symmetry.

The symmetry axis of PH_3 and NH_3 passes through P or N atom and is perpendicular to the plane containing all the three hydrogen atoms. The molecule has to be rotated by 120° around the axis to get an equivalent configuration. Thus these molecules have C_3 symmetry. Slmilarly planar BCl_3 molecule would also have C_3 symmetry.

Similarly IF_5 and benzene would have C_4 and C_6 symmetry respectively. On the other hand Thiophene would have C_2 symmetry. These molecules are shown in Fig. 9.2.



C_3 C_4 C_2 C_6

Fig. 9.2. Molecules with C_n symmetry.

The symmetry axis of a linear molecule like HCl coincides with the molecular axis and hence it possesses a C_∞ axis of symmetry. There are an infinite number of rotation operations about the symmetry axis which produce equivalent Configuration of the molecules.

9.1.2 PLANE OF SYMMETRY

It is defined as a plane through which reflections of all the atoms of the molecule produce an equivalent configuration of the molecule. For example, water molecule possesses two such planes (a) and (b), as shown in Fig. 9.3.

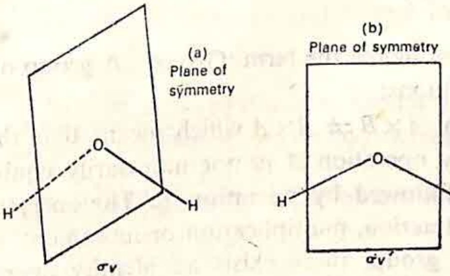


Fig. 9.3. Axes of symmetry of water molecule.

(b) is the molecular plane and (a) is perpendicular to it passing through the axis of symmetry. These are called vertical planes since these contain the C_2 axis.

The symbol for a symmetry plane is σ and for a vertical plane is σ_v. In order to differentiate between two such planes as (a) and (b), the molecular plane is represented by σ_v'.

9.1.3 CENTRE OF SYMMETRY OR INVERSION CENTRE

It is defined as the point through which a molecule may inverted so as to produce an equivalent configuration. It is denoted by i, which also indicates the operation of inversion of the molecule.

It should be noted that the water molecule does not possess such an element of symmetry. A regular octahedron possesses an inversion centre. CCl_4 would have no inversion Centre. A linear molecule AH_2 possesses an inversion centre which is the centre of atom A.

9.1.4 IDENTITY

The identity operation is associated with the symmetry operation which leaves the molecule intact thus producing an equivalent molecular configuration. It may be noted that this particular symmetry operation is trivial. However, it is mathematically necessary, from the view point of group theory. It is denoted by the symbol E.

These symmetry elements are used to classify the molecular shapes and molecular orbitals. For this purpose, group theory is of considerable help.

9.2 Group Theory

We shall first define the term 'Group'. A group obeys following four conditions:

i) In general $A \times B \neq B \times A$ which means that the operation B followed by operation A is not necessarily equivalent to the operation A followed by operation B. The operation could be addition, subtraction, multiplication or movement.

ii) In each group, there exists an identity operation E such that for any operation involving the group.

$$A \times E = E \times A = A$$

iii) For each operation A there exists in the group an inverse operation A^{-1} such that $A^{-1} \times A = A \times A^{-1} = E$.

iv) the associative law of Mathematics holds:

$$A \times (B \times C) = (A \times B) \times C$$

To illustrate the meaning of Group we shall give a few examples,

a) Set of integers 0, $\pm$ 1, $\pm$ 2, $\pm$ 3, $\pm$ 4 constitute a group with respect to binary operation of addition. For this group identity E is 0 and A^{-1} for an integer is the integer with an opposite sign. It is also obvious that (iii) holds for the set of integers and hence the set is a group.

b) A set of non-zero rational number 1, 2, 3, 4, . . . , $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ also form a group with respect to binary multiplication operation.

We will now show that the symmetry elements discussed above also constitute a group. We take the case of water for illustration.

H_2O has four symmetry operations as discussed earlier;

$$E,\ C_2,\ \sigma_v \text{ and } \sigma_v'$$

The operation of one vertical mirror plane σ_v followed by the operation of the other vertical mirror plane is equivalent to two-fold operations, that is,

$$\sigma_v' \times \sigma_v = C_2 \tag{9.1}$$

Similarily the successive operations of C_2 followed by σ_v yields the same result i.e. σ_v' operation so that

$$\sigma_v \times C_2' = \sigma_v' \tag{9.2}$$

Each of the four operation has its own inverse for example

$$\sigma_v \times \sigma_v = E \tag{9.3}$$

Just as the ordinary multiplication results are expressed by mathematical Tables 9.1(a) in the same way, we have group multi-

Table 9.1. Normal multiplication table and group multiplication table

	2	4	6	8
2 :	4	8	12	16
4 :	8	16	24	32
6 :	12	24	36	48
8 :	16	32	48	64

(a) Multiplication table

	E	C_2'	σ_v	σ_v'
E	E	C_2'	σ_v	σ_v'
C_2'	C_2'	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2'
σ_v'	σ_v'	σ_v	C_2'	E

(b) Group multiplication table

The table (b) contains the product $A \times B$ for the indicated operation. It may be noted that each symmetry operation is represented in each column and each row only once.

plication Table 9.1(b) which summarises the results of successive operation. The product operations for C_2 group are summarised in the form of Table 9.1(b). An ordinary mathematical multiplication table is given on the right hand side for comparision.

From the group multiplication table, it follows that

$$C'_2 E = C'_2 = E\, C'_2 \qquad \text{and so on}$$

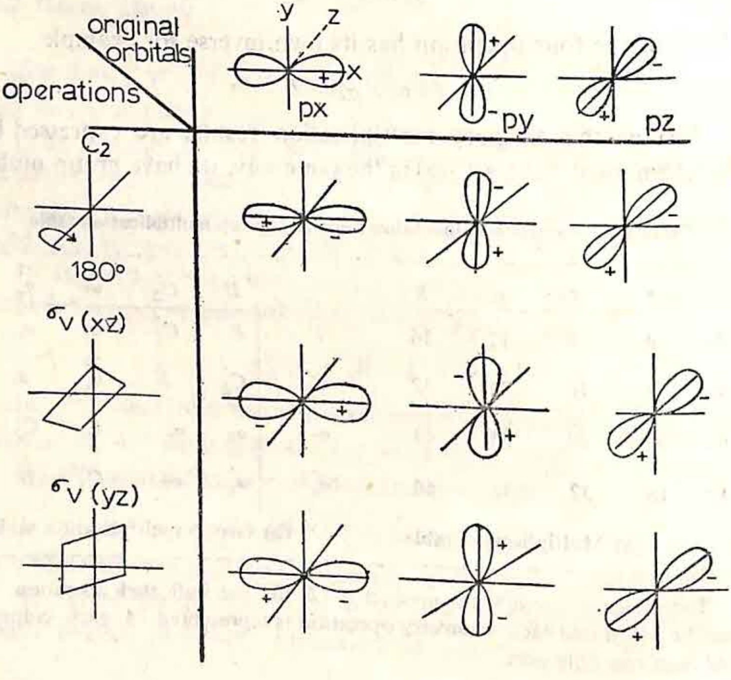
so that the operations are commutative.

The elements of symmetry of a molecule can be ascertained from its structure. This knowledge is of little use for the purpose under discussion. It is more important to consider the effect of the symmetry operations on the atomic or molecular orbitals.

9.3 Symmetry Operation of Orbitals

Let us consider the effect of symmetry operations on the valency orbitals of the oxygen atom in the water molecule. Since the 2s orbital of oxygen has spherical symmetry it will be unaltered by

Table 9.2. Multiplication table of p-orbitals



rotation or reflection with respect to its centre. The effect of the other operators on the three $2p$ orbitals are summarised in Table 9.2.

It can be seen that each operation restores each orbital to its original position, but sometimes with a change of sign. When an operator generates a new orbital identical in position and sign with the original, the effect of the operator is same as multiplying the original orbital by $+1$. Similarly when the operator restores the orbital to its original position, but with a change of sign, this is the same thing as multiplying the orbital by -1. These numbers are simple examples of matrices each of which represents the action of operator. The operations shown in Table 9.2 can be written as follows:

$$p_y' = C_2\,(p_y) = (-1)\,p_y \tag{9.4}$$

$$p_z'' = \sigma_v\,(p_z) = (+1)\,p_z \tag{9.5}$$

The effect of the operators of the C_{2v} group on the oxygen orbitals has been summarised in Table 9.3

Table 9.3. Group multiplication table for oxygen orbital

	E	C_2	$\sigma_v\,(xz)$	$\sigma_v'\,(yz)$
$2s$	$+1$	$+1$	$+1$	$+1$
$2p_x$	$+1$	-1	$+1$	-1
$2p_y$	$+1$	-1	-1	$+1$
$2p_z$	$+1$	$+1$	$+1$	$+1$

9.4 Application of Group Theory to Simple Molecules

It is possible to classify the orbitals of a bent molecule (AH_2) in terms of whether they are symmetric or antisymmetric to the four symmetry operations associated with the elements of the symmetry of the molecule. There are in fact, only four different classes of orbitals possible which are independent of each other in this respect. These are given in Table 9.4.

As in the former case $+1$ denoted that the orbital is symmetric to the particular operation and -1 denotes that the orbital is antisymmetric to the particular operation. It follows from the comparison of the two tables that the symmetry character of $2s$

Table 9.4. Character table of molecular orbitals of AH_2

Symmetry symbol	E	C_2	$\sigma_v\ (xz)$	$\sigma'_v\ (yz)$
a_1	+1	+1	+1	+1
a_2	+1	+1	−1	−1
b_1	+1	−1	+1	−1
b_2	+1	−1	−1	+1

and $2p_z$ orbitals is a_1, whereas that for $2p_x$ and $2p_y$ orbitals, the symmetry characters are b_1 and b_2.

Thus, the symmetry character of atomic orbitals involved in bonding in bent AH_2 molecule (90°) are as follows:

	Orbital	Symmetry character
Central atom	s	a_1
	$2p_x$	b_1
	$2p_y$	b_2
	$2p_z$	a_1

	Orbital	Symmetry character
Hydrogen atom	$G_1\ (S)$	a_1
	$G_2\ (S)$	b_2

where G_1 and G_2 denote the linear combination of wave-functions of the two hydrogen atoms. With the above knowledge about the b_2 symmetry character of orbitals, we can at once decide which orbitals should be excluded from participation in any combination. It is obvious that out of all orbitals, the symmetry character of p_x orbital of the central atom does not tally with the symmetry character of the hydrogen atom. Therefore, p_x orbital is a non-bonding orbital.

Hence following linear combination of atomic orbitals may be written

$$\psi'_1 = \frac{1}{\sqrt{2}}\ (\psi_{p_z}\ (A) + G_1) \tag{9.6}$$

$$\psi'_5 = \frac{1}{\sqrt{2}}\ (\psi_{p_z}\ (A) - G_1) \tag{9.7}$$

$$\psi'_2 = \frac{1}{\sqrt{2}}\ (\psi_{p_y}\ (A) + G_2) \tag{9.8}$$

$$\psi'_6 = \frac{1}{\sqrt{2}} (\psi_{p_y}(A) - G_2) \tag{9.9}$$

The non-bonding orbitals are the following:

$$\psi'_3 = \psi_s\ (A) \tag{9.10}$$

$$\psi'_4 = \psi_{p_x}(A) \tag{9.11}$$

In writing the above M.O., only orbitals having similar symmetry character and energy have been combined.

Bonding characters of molecular orbitals in a bent AH_2 molecule are summarised below:

	Orbital	Character	Symmetry
↑	ψ'_6	antibonding	$\bar{b}_2$
	ψ'_5	antibonding	$\bar{a}_2$
	ψ'_4	non-bonding	b_1
E	ψ'_3	non-bonding	a_1
	ψ'_2	bonding	b_2
	ψ'_1	bonding	a_1

The above example demonstrates in a simple way the application of ideas of group theory in writing down the molecular orbitals.

CHAPTER 10

Large Organic Molecules

We shall now discuss M.O. method for treating large organic molecules where we have to depend on methods which make use of approximations. Electron density, bond order and free valence can be calculated using such method. Following mathematical steps are essentially involved in this method.

1) The molecular orbital ϕ is represented by a linear combination (LCAO) of the atomic orbitals $\chi_1, \chi_2, \ldots,$

$$\phi = c_1 \chi_1 + c_2 \chi_2 + \tag{10.1}$$

2) The coefficients of the atomic orbitals (viz. $c_1, c_2, \ldots$) are so chosen that the energy $E = \int \phi H \phi \, d\tau / \int \phi^2 \, d\tau$ is minimum. In order to achieve this objective $\frac{\partial E}{\partial c_i}$ is put equal to zero for all values of i.

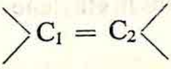
3. The resulting secular equations are solved to obtain the values of E which can be used for evaluating the coefficients. Knowing these coefficients molecular orbitals corresponding to energy E_i can be explicitly written.

We shall illustrate the use of M.O. calculations for ethylene, butadiene and benzene molecules. The calculations become increasingly difficult with the increase in the number of atoms in the molecule. However, the computational labour can be reduced by using symmetry considerations and ideas of group theory or by using computers. In applying M.O. theory to π-electron systems considerable simplification is achieved by considering only orbitals having requisite symmetry. It is only necessary to consider the linear combination of π-electrons alone since σ-electrons have different symmetry as we have seen earlier. This approach is called Hackel Molecular Orbital theory (HMO). However, accurate calculations indicate that it is not quite correct to ignore σ-electrons. In spite of this the simplified approach yields useful results.

We shall first discuss the molecular orbital treatment of ethylene.

10.1 Ethylene

The ethylene molecule contains twelve valence electrons. Out of these, ten form σ-bonds with which we will not be concerned. We will consider the remaining two π-electrons which form a single π-bond between the two carbon atoms of ethylene,



If χ_1 denotes the p_z atomic orbital on carbon one and χ_2 on carbon two, then a linear combination of these two p_z atomic orbitals will be represented by a molecular orbital thus:

$$\phi = c_1 \chi_1 + c_2 \chi_2 \tag{10.2}$$

The energy E of the molecular orbital is given by,

$$E = \frac{\int (c_1 \chi_1 + c_2 \chi_2)\, H\, (c_1 \chi_1 + c_2 \chi_2)\, d\tau}{\int (c_1 \chi_1 + c_2 \chi_2)^2\, d\tau} \tag{10.3}$$

The integral on the r. h. s of equation (10.3) on expansion would involve integrals of the type $\int \chi_1 H \chi_1\, d\tau$, $\int \chi_1 H \chi_2\, d\tau$ and $\int \chi_1 \chi_2\, d\tau$. For many purposes, it is sufficient to present the results in terms of these integrals. We discuss below some of the properties of these

We put,
$$\int \chi_1 H \chi_1\, d\tau = \alpha_1$$

$$\int \chi_2 H \chi_2\, d\tau = \alpha_2 \tag{10.4}$$

where α_1 and α_2 are coulomb intgrals.

Further, we put

$$\int \chi_1 H \chi_2\, d\tau = \beta_{12}$$

$$\int \chi_2 \, H \, \chi_1 \, d\tau = \beta_{21} \tag{10.5}$$

$$\int \chi_1 \, \chi_2 \, d\tau = S = \int \chi_2 \, \chi_1 \, d\tau$$

where β and S are respectively called resonance and overlap integrals.

The Coulomb integral α_1 represents the energy of electron belonging to carbon atom one. This energy is due to this attraction between the electron and the atomic core of carbon one. At an infinite distance from the carbon atom the energy would be zero accordingly α_1 and α_2 at a finite distance from the atom are less than zero so that

$$\alpha_1 < 0 \quad \text{and} \quad \alpha_2 < 0$$

Since the two carbon atoms in ethylene are equivalent it is reasonable to put

$$\alpha_1 = \alpha_2 = \alpha; \; \beta_{12} = \beta_{21} = \beta \tag{10.6}$$

Such a relationship is not restricted to the case of two equivalent atoms alone but is valid in general. Further, it can be shown that

$$\beta_{12} < 0 \quad \text{and} \quad \beta_{21} < 0$$

The overlap integral S indicates the degree of overlap of two atomic orbitals χ_1 and χ_2. It can have values between 0 and 1. For adjacent carbon atoms in benzene S is found to be equal to 0.25. However, S decreases rapidly as the distance between the atoms increases.

Now, we proceed with the explicit evaluation of E. This we have from equations (10.3) and (10.6),

$$\begin{aligned} E &= \frac{\int (c_2 \, c_1^2 \, \chi_1 H \chi_1 + c_1 c_2 \, \chi_1 H \chi_2 + c_2 c_1 \, \chi_2 H \chi_1 + c_2^2 \, \chi_2 H \chi_2) \, d\tau}{\int (c_1^2 \, \chi_1^2 + c_1 c_2 \chi_1 \chi_2 + c_2 c_1 \chi_2 \chi_1 + c_2^2 \chi_2^2) \, d\tau} \\ &= \frac{c_1^2 \alpha + c_1 c_2 \beta + c_2 c_1 \beta + c_2^2 \, \alpha}{c_1^2 + c_1 c_2 \, S + c_2 c_1 \, S + c_2^2} \\ &= \frac{[c_1^2 + c_2^2] \, \alpha + 2 \, c_1 c_2 \beta}{c_1^2 + 2 \, c_1 c_2 \, S + c_2^2} \end{aligned} \tag{10.7}$$

or

$$E \, [c_1^2 + 2 \, c_1 c_2 \, S + c_2^2] = (c_1^2 + c_2^2) \, \alpha + 2 \, c_1 c_2 \beta \tag{10.8}$$

Applying the condition for minima, i.e.

$$\frac{\partial E}{\partial c_1} = 0 \quad \text{and} \quad \frac{\partial E}{\partial c_2} = 0 \tag{10.9}$$

on differentiation of equation (10.8) with respect to c_1 and using equation (10.9) we have,

$$\frac{\partial E}{\partial c_1}[c_1^2 + 2c_1 c_2 S + c_2^2] + E[2c_1 + 2c_2 S] = 2c_1\alpha + 2c_2\beta$$

or
$$E(2c_1 - 2c_2 S) = 2c_1\alpha = 2c_2\beta$$

or
$$c_1(\alpha - E) + c_2(\beta - ES) = 0 \tag{10.10}$$

Similarly differentiating equation (10.9) with respect to c_2 and putting $\partial E/\partial c_2 = 0$, we get

$$\frac{\partial E}{\partial c_2}[c_1^2 + 2c_1 c_2 S + c_2^2] + E[2c_1 S + 2c_2] = 2c_2\alpha + 2c_1\beta$$

or
$$E(2\,c_1\,S + 2\,c_2) = 2\,c_2\alpha + 2\,c_1\beta$$

or
$$c_1(\beta - ES) + c_2(\alpha - E) = 0 \tag{10.11}$$

For the sake of simplicity we assume that $S = 0$.
The above equations then yields,

$$c_1(\alpha - E) + c_2\,\beta = 0$$
$$c_1\,\beta + c_2(\alpha - E) = 0 \tag{10.12}$$

These equations are satisfied if $c_1 = c_2 = 0$. If this is not so, then

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \tag{10.13}$$

The above is a secular equation. Thus, we have

$$(\alpha - E)^2 - \beta^2 = 0$$

or
$$(\alpha - E + \beta)(\alpha - E - \beta) = 0 \tag{10.14}$$

Consequently, one will get the two roots E_1 and E_2 given by

$$E_1 = \alpha + \beta \tag{10.15}$$

and
$$E_2 = \alpha - \beta \tag{10.16}$$

On putting the value of E_1 in equation (10.12), we have

$$c_1\,\beta - c_2\,\beta = 0 \tag{10.17}$$

Since $\beta \neq 0$, we have $c_1 = c_2$

Further, the molecular orbital must obey the normalisation condition so that

$$\int \phi^2 \, d\tau = \int (c_1 \chi_1 + c_2 \chi_2)^2 \, d\tau = 1$$

or
$$c_1^2 \int \chi_1^2 \, d\tau + c_2^2 \int \chi_2^2 \, d\tau + 2 c_1 c_2 \int \chi_1 \chi_2 \, d\tau = 1 \quad (10.18)$$

By using the normalisation condition for atomic orbitals, we have from equation (10.18)

$$c_1^2 + c_2^2 + 2 c_1 c_2 S = 1 \quad (10.19)$$

Further since $S = 0$, we get

$$c_1^2 + c_2^2 + 1 \quad (10.20)$$

Hence it follows that

$$c_1 = c_2 = \frac{1}{\sqrt{2}} \quad (10.21)$$

The molecular orbital related to $E_1 = \alpha + \beta$ will be called ϕ_1. Hence,

$$\phi_1 = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2) \quad (10.22)$$

Similarly the molecular orbital associated with $E_2 = \alpha - \beta$ would be called ϕ_2 which can be shown to be given by

$$\phi_2 = \frac{1}{\sqrt{2}} (\chi_1 - \chi_2) \quad (10.23)$$

Thus, we have two molecular orbitals ϕ_1 and ϕ_2 with energies E_1 and E_2 respectively. These are pictorially depicted in Fig. 10.1.

The two π-electrons of ethylene would occupy the lowest molecular orbital ϕ. Thus total energy W of this state is given by

$$W = 2 E_1 = 2\alpha + 2\beta \quad (10.24)$$

In excited states one or two of the π-electrons may be promoted to the orbital ϕ_2, then the energy of the excited state would be either

$$W = E_1 + E_2 = 2\alpha \quad \text{or} \quad W = 2E_2 = 2\alpha - 2\beta \quad (10.25)$$

Pictorially it can be represented as,

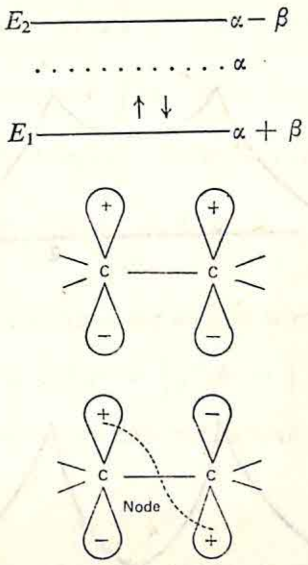


Fig. 10.1. Orbital picture of MO's of ethylene.

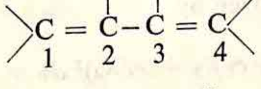
10.1.1 MOLECULAR ORBITALS AND CHARGE DISTRIBUTION IN ETHYLENE

We can plot ϕ_1^2 and ϕ_2^2 as a function of distance in the following manner using equations (10.22) and (10.23). This is done in Fig. 10.2. In the diagram, 1 and 2 refer to the two carbon nuclei

There is a marked difference between ϕ_1^2 and ϕ_2^2 regarding the behaviour of these functions at the middle point of the carbon-carbon bond where ϕ_2^2 is zero. Consequently ϕ_1 is a bonding-orbital and ϕ_2 is an anti-bonding orbital.

10.2 Butadiene

Butadiene has four π-electrons which move in the molecular framework of four carbon atom. We will ignore the electrons forming σ-bonds and will consider four π-electrons only.



The four carbon atoms of the butadiene molecule 1, 2, 3 and 4 have 2 *pz* atomic orbitals denoted by χ_1, χ_2, χ_3 and χ_4. The mole-

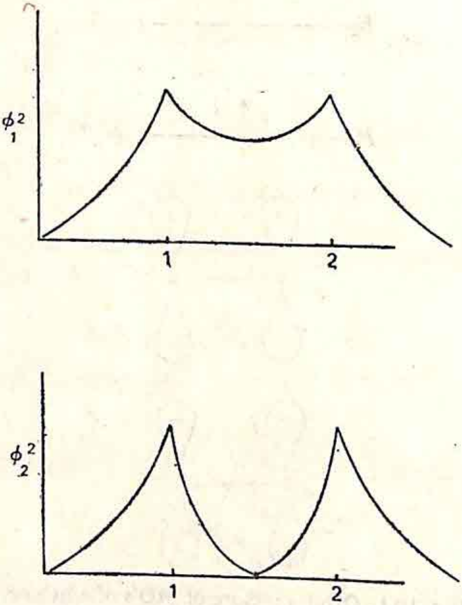


Fig. 10.2. Probability distribution functions of molecular orbitals of ethylene (abcissa represents this internuclear distance).

cular orbital ϕ is represented as usual by a linear combination of these atomic orbitals as follows,

$$\phi = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4 \tag{10.26}$$

We will now evaluate the coefficients c_1, c_2, c_3, c_4 and the energy E associated with each orbital ϕ. In order to obtain E, we shall minimise the following expression,

$$E = \frac{\int (c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4)\, H\, (c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4)\, d\tau}{\int (c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4)^2\, d\tau} \tag{10.27}$$

The denominator is given by

$$\int (c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4)^2\, d\tau$$
$$= c_1^2 \int \chi_1^2\, d\tau + c_2^2 \int \chi_2^2\, d\tau + c_3^2 \int \chi_3^2\, d\tau + c_4^2 \int \chi_4^2\, d\tau$$

$$+ c_1 c_2 \int \chi_1 \chi_2 \, d\tau + c_1 c_3 \int \chi_1 \chi_3 \, d\tau + c_1 c_4 \int \chi_1 \chi_4 \, d\tau$$

$$+ c_2 c_1 \int \chi_2 \chi_1 \, d\tau + c_2 c_3 \int \chi_2 \chi_3 \, d\tau + c_2 c_4 \int \chi_2 \chi_4 \, d\tau$$

$$+ c_3 c_1 \int \chi_3 \chi_1 \, d\tau + c_3 c_2 \int \chi_3 \chi_2 \, d\tau + c_3 c_4 \int \chi_3 \chi_4 \, d\tau$$

$$+ c_4 c_1 \int \chi_4 \chi_1 \, d\tau + c_4 c_2 \int \chi_4 \chi_2 \, d\tau + c_4 c_3 \int \chi_4 \chi_3 \, d\tau \tag{10.28}$$

The normalisation condition for atomic orbitals yields

$$\int \chi_1^2 \, d\tau = \int \chi_2^2 \, d\tau = \int \chi_4^2 \, d\tau = \int \chi_4^2 \, d\tau = 1 \tag{10.29}$$

We denote the overlap integrals between any two atoms r and s by S_{rs} given by

$$S_{rs} = \int \chi_r \chi_s \, d\tau \tag{10.30}$$

We further assume

1) For two adjacent atoms:

$$S_{12} = S_{21} = S_{23} = S_{32} = S_{34} = S_{43} = S \tag{10.31}$$

2) For two non-adjacent atoms

$$S_{13} = S_{31} = S_{14} = S_{41} = S_{24} = S_{42} = 0 \tag{10.32}$$

Thus, the denominator becomes

$$\int \phi^2 \, d\tau = c_1^2 + c_2^2 + c_3^2 + c_4^2 + 2(c_1 c_2 + c_2 c_3 + c_3 c_4) S \tag{10.33}$$

For the sake of simplicity, we put $S = 0$, as assumed earlier so that

$$\int \phi^2 \, d\tau = c_1^2 + c_2^2 + c_3^2 + c_4^2 \tag{10.34}$$

The numerator of r.h.s. of equation (10.27) is given by

$$\int (c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4) \, H \, (c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4) \, d\tau$$

$$= c_1^2 \int \chi_1 H \chi_1 \, d\tau + c_1 c_2 \int \chi_1 H \chi_2 \, d\tau + c_1 c_3 \int \chi_1 H \chi_3 \, d\tau$$

$$+ c_1 c_4 \int \chi_1 H \chi_4 \, d\tau$$

$$+ c_2 c_1 \int \chi_2 H \chi_1 \, d\tau + c_2^2 \int \chi_2 H \chi_2 \, d\tau + c_2 c_3 \int \chi_2 H \chi_3 \, d\tau$$

$$+ c_2 c_4 \int \chi_2 H \chi_4 \, d\tau$$

$$+ c_3 c_1 \int \chi_3 H \chi_1 \, d\tau + c_3 c_2 \int \chi_3 H \chi_2 \, d\tau + c_3^2 \int \chi_3 H \chi_3 \, d\tau$$

$$+ c_3 c_4 \int \chi_4 H \chi_4 \, d\tau$$

$$+ c_4 c_1 \int \chi_4 H \chi_1 \, d\tau + c_4 c_2 \int \chi_4 H \chi_2 \, d\tau + c_4 c_3$$

$$\int \chi_4 H \chi_3 \, d\tau + c_4^2 \int \chi_4 H \chi_4 \, d\tau \qquad (10.35)$$

We know that

$$\int \chi_1 H \chi_1 \, d\tau = \int \chi_2 H \chi_2 \, d\tau = \int \chi_3 H \chi_3 \, d\tau =$$

$$\int \chi_4 H \chi_4 \, d\tau = \alpha \qquad (10.36)$$

This is, of course, a crude approximation because the end atoms are obviously different from the central atoms. Further, we have

$$\beta_{12} = \int \chi_1 H \chi_2 \, d\tau = \int \chi_2 H \chi_1 \, d\tau = \beta_{21}, \qquad (10.37)$$

$$\beta_{12} = \beta_{21} = \beta_{23} = \beta_{32} = \beta_{34} = \beta_{43} = \beta \qquad (10.38)$$

and

$$\beta_{13} = \beta_{31} = \beta_{14} = \beta_{41} = \beta_{24} = \beta_{42} = 0 \qquad (10.39)$$

for non-adjacent atoms. Thus,

the numerator $= \alpha\,(c_1^2 + c_2^2 + c_3^2 + c_4^2) + 2\beta +$

$$(c_1 c_2 + c_2 c_3 + c_3 c_4) \qquad (10.40)$$

Hence, equation (10.27) is reduced to

$$E\,(c_1^2 + c_2^2 + c_3^2 + c_4^2) = \alpha\,(c_1^2 + c_2^2 + c_3^2 + c_4^2)$$

$$+ 2\beta\,(c_1 c_2 + c_2 c_3 + c_3 c_4) \qquad (10.41)$$

On differentiating E with respect to c_1 we have,

$$\frac{\partial E}{\partial c_1}\,(c_1^2 + c_2^2 + c_3^2 + c_4^2) + c_1 E = 2c_1 \alpha + 2c_2 \beta \qquad (10.42)$$

Now putting $\dfrac{\partial E}{\partial c_1} = 0,$

we get

$$c_1 E = c_1 \alpha + c_2 \beta \qquad (10.43)$$

Similarly on differentiating equation (10.41) with respect to c_2, c_3 and c_4 and then putting $\frac{\partial E}{\partial c_2} = 0$; $\frac{\partial E}{\partial c_3} = 0$ and $\frac{\partial E}{\partial c_4} = 0$ respectively, we get

$$c_2 E = c_2 + c_1 \beta + c_3 \beta \tag{10.44}$$

$$c_3 E = c_3 \alpha + c_2 \beta + c_4 \beta \tag{10.45}$$

and

$$c_4 E = c_4 \alpha + c_3 \beta \tag{10.46}$$

On rearranging following four equations are obtained,

$$c_1 (\alpha - E) + c_2 \beta = 0 \tag{13.47}$$

$$c_1 \beta + c_2 (\alpha - E) + c_3 \beta = 0 \tag{10.48}$$

$$c_2 \beta + c_3 (\alpha - E) + c_4 \beta = 0 \tag{10.49}$$

$$c_3 \beta + c_4 (\alpha - E) = 0 \tag{10.50}$$

The solution of these equations lead to,

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.51}$$

Dividing all the terms in the determinant by β and putting $\frac{\alpha - E}{\beta} = \omega$ equation (10.51) yields

$$\begin{vmatrix} \omega & 1 & 0 & 0 \\ 1 & \omega & 1 & 0 \\ 0 & 1 & \omega & 1 \\ 0 & 0 & 1 & \omega \end{vmatrix} = 0$$

On expanding the above determinant by the usual procedure we get the following secular equation

$$\omega^4 - 3\omega^2 + 1 = 0$$

or

$$(\omega^2 + \omega - 1)(\omega^2 - \omega - 1) = 0 \tag{10.52}$$

or

$$\omega = \frac{-1 \pm \sqrt{5}}{2} \quad \text{or} \quad \frac{1 \pm \sqrt{5}}{2} \tag{10.53}$$

The four roots are as follows,

$\omega_1 = -1.618$; $\omega_2 = -0.618$; $\omega_3 = +0.618$ and $\omega_4 = 1.618$,

where $\sqrt{5} = 2.236068$.

By substituting the appropriate values of ω, we get the following four equations,

$$E_1 = \alpha + 1.618\,\beta \tag{10.54}$$

$$E_2 = \alpha + 0.618\,\beta \tag{10.55}$$

$$E_3 = \alpha - 0.618\,\beta \tag{10.56}$$

$$E_4 = \alpha - 1.618\,\beta \tag{10.57}$$

and $c_2 = c_3$

Using the normalisation condition for the orbitals, we get,

$$2\,(c_1^2 + 1.618\,c_1^2) = 1$$

or
$$c_1 = c_4 = 0.3717$$

and
$$c_2 = c_3 = 0.6015 \tag{10.58}$$

The molecular orbital ϕ_1 associated with E_1 is given by

$$\phi_1 = 0.3717\,\chi_1 + 0.6015\,\chi_2 + 0.6015\,\chi_3 + 0.3717\,\chi_4 \tag{10.59}$$

Similarly one can obtain the coefficients of the other molecular orbitals. The results are given in Table 10.1. Various orbitals are depicted in Fig. 10.3.

Table 10.1: Energies of different orbitals of butadiene

Molecular orbital	Wave function	Symmetry	Energy
ϕ_1	$0.3717\,\chi_1+0.6015\,\chi_2$ $+0.6015\,\chi_3+0.3717\,\chi_4$	Symmetric (*S*)	$E_1=\alpha + 1.6180\,\beta$
ϕ_2	$0.6015\,\chi_1+0.3717\,\chi_2$ $-0.3717\,\chi_3-0.6015\,\chi_4$	Antisymmetric (*A*)	$E_2=\alpha+0.6180\,\beta$
ϕ_3	$0.6015\,\chi_1-0.3717\,\chi_2$ $-0.3717\,\chi_3+0.6015\,\chi_4$	Symmetric (*S*)	$E_3=\alpha-0.6180\,\beta$
ϕ_4	$0.3717\,\chi_1-0.6015\,\chi_2$ $+0.6015\,\chi_3-0.3717\,\chi_4$	Anti Symmetric (*A*)	$E_4=\alpha-1.6180\,\beta$

As pointed out earlier, if all the π-electrons are delocalised, then the energy W is equal to $4\,\alpha + 4.72\,\beta$.

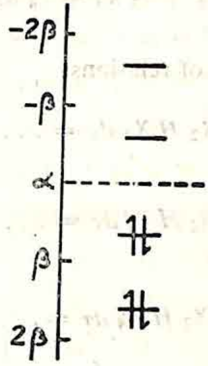


Fig. 10.3. HMO π energy level diagram for butadiene.

However when the electrons are localised in bonds $c_1 - c_2$ and $c_3 - c_4$, the hypothetical energy W' would be equal to twice the energy of ethylene i.e.,

$$W' = 2\ W\,[\text{ethylene}] \tag{10.60}$$

so that

$$W' = 4\,\alpha + 4\,\beta \tag{10.61}$$

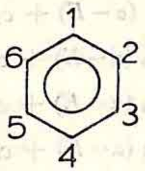
The difference $W' - W$ is the resonance energy W_R of butadiene and hence,

$$W_R = W' - W = 0.4720\,(-\beta) \tag{10.62}$$

W_R is also called delocalisation energy.

We will discuss the M.O. treatment of benzene.

10.3. Benzene



Benzene constitutes a system of six π-electron moving in a molecular framework of six equivalent c atoms. If we denote the atomic orbitals associated with each of these atoms by χ_1 $\chi_2, \ldots$ χ_3, respectively, the molecular orbital ϕ, can be represented by

$$\phi = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4 + c_5 \chi_5 + e_6 \chi_6 \tag{10.63}$$

Using the following set of relations:

$$\int \chi_1 H \chi_1 \, d\tau = \int \chi_2 H \chi_2 \, d\tau = \ldots = \int \chi_6 H \chi_6 \, d\tau = \alpha \tag{10.64}$$

$$\int \chi_1 H \chi_2 \, d\tau = \int \chi_2 H \chi_3 \, d\tau = \ldots = \int \chi_5 H \chi_6 \, d\tau = \beta \tag{10.65}$$

$$\int \chi_1 H \chi_3 \, d\tau = \int \chi_2 H \chi_4 \, d\tau = \ldots = 0 \tag{10.66}$$

$$\int \chi_1 \chi_2 \, d\tau = \int \chi_1 \chi_3 \, d\tau = \int \chi_1 \chi_4 \, d\tau = \ldots = S = 0 \tag{10.67}$$

the energy E can be expressed as

$$E = \frac{\alpha\,(c_1^2 + c_2^2 + \ldots c_6^2) + 2\,(c_1 c_2 + c_2 c_3 + \ldots + c_6 c_1)\,\beta}{c_1^2 + c_2^2 + \ldots + c_6^2} \tag{10.68}$$

The parameters α and β being given, E is a function of only six variables $c_1, c_2, \ldots, c_6$. From the condition that E must have a minimum value we obtain six relation

$$\frac{\partial E}{\partial c_1} = 0\,; \frac{\partial E}{\partial c_2} = 0, \ldots, \frac{\partial E}{\partial c_6} = 0 \tag{10.69}$$

Thus, we get six simultaneous equations

$$c_1 (\alpha - E) + c_2 \beta + c_6 \beta = 0 \tag{10.70}$$

$$c_1 \beta + c_2 (\alpha - E) + c_3 \beta = 0 \tag{10.71}$$

$$c_2 \beta + c_3 (\alpha - E) + c_4 \beta = 0 \tag{10.72}$$

$$c_3 \beta + c_4 (\alpha - E) + c_5 \beta = 0 \tag{10.73}$$

$$c_4 \beta + c_5 (\alpha - E) + c_6 \beta = 0 \tag{10.74}$$

$$c_1 \beta + c_5 \beta + c_6 (\alpha - E) = 0 \tag{10.75}$$

By putting $\omega = \dfrac{\alpha - E}{\beta}$, these reduce to

$$c_1 \omega + c_2 + c_6 = 0 \tag{10.76}$$

$$c_1 + c_2\,\omega + c_3 = 0 \tag{10.77}$$

$$c_2 + c_3\,\omega + c_4 = 0 \tag{10.78}$$

$$c_3 + c_4\,\omega + c_5 = 0 \tag{10.79}$$

$$c_4 + c_5\,\omega + c_6 = 0 \tag{10.80}$$

$$c_1 + c_5 + c_6\,\omega = 0 \tag{10.81}$$

The solution of these simultaneous equations lead to

$$\begin{vmatrix} \omega & 1 & 0 & 0 & 0 & 1 \\ 1 & \omega & 1 & 0 & 0 & 0 \\ 0 & 1 & \omega & 1 & 0 & 0 \\ 0 & 0 & 1 & \omega & 1 & 0 \\ 0 & 0 & 0 & 1 & \omega & 1 \\ 1 & 0 & 0 & 0 & 1 & \omega \end{vmatrix} = 0$$

By solving the determinant we finally obtain a sixth order equation,

$$\omega^6 - 6\,\omega^4 + 9\,\omega^2 - 4 = 0 \tag{10.82}$$

By putting $\omega^2 = \chi$ we get,

$$\chi^3 - 6\,\chi^2 + 9\,\chi - 4 = 0 \tag{10.83}$$

or

$$(\chi - 1)^2\,(\chi - 4) = 0 \tag{10.84}$$

Consequently,

$$\omega = \pm\,1 \;\text{(two times)} \tag{10.85}$$

$$\omega = \pm\,2 \tag{10.86}$$

Therefore the energy values of the molecular orbitals in order of increasing energy are

$$E_1 = \alpha + 2\,\beta \tag{10.87}$$

$$E_2 = E_3 = \alpha + \beta \tag{10.88}$$

$$E_4 = E_5 = \alpha - \beta \tag{10.89}$$

and

$$E_6 = \alpha - 2\,\beta \tag{10.90}$$

As β is a negative quantity, the lowest energy is $\alpha + 2\,\beta$ and the highest $\alpha - 2\,\beta$, thus

$$E_1 < E_2 = E_3 < E_4 = E_5 < E_6$$

The normalisation condition leads to

$$\int \phi^2 \, d\tau = c_1^2 + c_2^2 + c_3^2 + \ldots c_6^2 = 1 \qquad (10.91)$$

Let us denote the coefficients of the molecular orbital associated with energy E_1 as c_{11}, c_{12}, c_{13}, c_{14}, c_{15} and c_{16}. By substituting $E_1 = \alpha + 2\beta$ in the six equations obtained earlier, we get finally

$$c_{11} = c_{12} = \ldots = c_{16} \qquad (10.92)$$

Using this result in equation (10.101), we get,

$$c_{11} = c_{12} = \ldots = c_{16} = \frac{1}{\sqrt{6}} \qquad (10.93)$$

Hence, the M.O. ϕ_1 associated with E_1 is given by

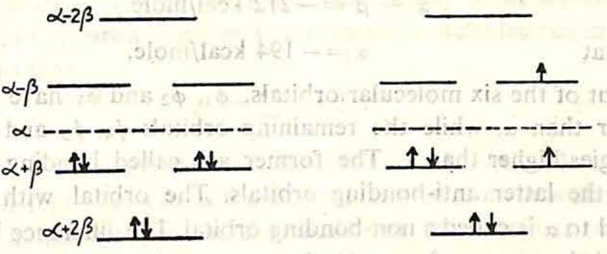
$$\phi_1 = \frac{1}{\sqrt{6}} (\chi_1 + \chi_2 + \ldots + \chi_6) \qquad (10.94)$$

Similarly all other M.O.'s can be determined. These and the corresponding energies are given in Table 10.2

Table 10.2 Molecular orbitals and energies of benzene

Energy E_1	M.O.
$E_1 = \alpha + 2\beta$	$\phi_1 = \frac{1}{\sqrt{6}} (\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6)$
$E_2 = \alpha + \beta$	$\phi_2 = \frac{1}{\sqrt{12}} (2\,\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6)$
$E_3 = \alpha + \beta$	$\phi_3 = \frac{1}{\sqrt{4}} (\chi_2 + \chi_3 + \chi_5 - \chi_6)$
$E_4 = \alpha - \beta$	$\phi_4 = \frac{1}{\sqrt{4}} (\chi_2 - \chi_3 + \chi_5 - \chi_6)$
$E_5 = \alpha - \beta$	$\phi_5 = \frac{1}{\sqrt{12}} (2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6)$
$E_6 = \alpha - 2\beta$	$\phi_6 = \frac{1}{\sqrt{6}} (\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6)$

One must note that both ϕ_2 and ϕ_3 have the same energy $E = \alpha - \beta$. Because of this double degeneracy there is freedom of choice of molecular orbitals. The energy level diagrams of the ground state and excited state of benzene are given below.



(a) Ground State (b) Excited State

Fig. 10.4. Energy level diagram for MOs of benzene.

We can now assign the six electrons to various molecular orbitals $\phi_1, \phi_2, \ldots, \phi_6$. In the ground state, two electrons will first occupy the lowest orbital ϕ_1 with energy $(\alpha + 2\beta)$, next two electrons would occupy the second lowest orbital ϕ_2 having energy $(\alpha + \beta)$ and the remaining two electrons would occupy ϕ_3 orbital having the energy $(\alpha + \beta)$.

The total energy W of these six electrons is therefore given by

$$W = 2\,E_1 + 2\,E_2 + 2\,E_3 = 6\,\alpha + 8\beta \qquad (10.95)$$

If the six π-electrons in benzene form three double bonds as described by a Kekule structure, its energy will be roughly equal to the energy of three molecules of ethylene, i.e.,

$$W' = 3\,(2\,\alpha + 2\beta) = 6\,\alpha + 6\beta \qquad (10.96)$$

Thus by the M.O. method the resonance energy W_R of benzene is given by

$$W_R = W' - W = (6\,\alpha + 6\beta) - (6\,\alpha + 8\beta) = -2\beta \qquad (10.97)$$

Since, β is a negative quantity, W_R has a positive sign and is sometimes called the delocalisation Energy. Thus, the six π-electrons in benzene belong to the non-localised orbitals extending over the whole molecular framework and W_R represents the energy of such delocalisation. We can estimate β from a knowledge of delocalisation energy. Thus, β is found to be -18 kcal/mole.

We can estimate α as follows. The first ionisation potential of benzene is equal to 9.21 eV or 212 kcal/mole. This can be roughly regarded as equivalent to the amount of energy which is needed to remove one π-electron from the highest occupied molecular orbital i.e.

$$\alpha + \beta = -212 \text{ kcal/mole}$$

so that
$$\alpha = -194 \text{ kcal/mole.}$$

Out of the six molecular orbitals, ϕ_1, ϕ_2 and ϕ_3 have energies lower than α, while the remaining orbitals ϕ_4, ϕ_5 and ϕ_6 have energies higher than α. The former are called bonding orbitals and the latter anti-bonding orbitals. The orbital with energy equal to α is called a non-bonding orbital. The difference between α and the energy of an orbital represents the bonding energy of the orbital. For example, the M.O. ϕ_1 of benzene has an energy $E = \alpha + 2\beta$, hence the bonding energy of this orbital is $\alpha - (\alpha + 2\beta) = -2\beta$.

If we assume that six π-electrons are localised on six carbon atoms, i.e., one electron on each carbon atom then the resulting energy will be 6 α. The difference between 6 α and the total energy W is the total bonding energy W_B so that

$$W_B = 6\,\alpha - W = -8\beta \tag{10.98}$$

We shall now illustrate how some of the molecular properties are estimated by M.O. method.

10.4. Electron Density

It is of considerable chemical interest to calculate the electron density at different carbon atoms in the molecules. We know that

$$\begin{aligned}\int \psi^2\, d\tau &= \int \sum (c_r\, \phi_r)^2\, d\tau \\ &= \int \sum_r c_r^2\, \phi_r^2\, d\tau + \int \sum_r \sum_{s \neq r} c_r\, c_s\, \phi_r\, \phi_s\, d\tau\end{aligned} \tag{10.99}$$

where ϕ_r and ϕ_s are the wave-function of the π-electron associated with any carbon atoms r and s.

On account of orthogonality theorem,

$$\int \phi_r\, \phi_s = 0 \quad \text{for} \quad r \neq s \tag{10.100}$$

Therefore,

$$\begin{aligned}\int \chi^2\, d\tau = \int \sum c_r^2\, \phi_r^2\, d\tau &= \sum c_r^2 \int \phi_r^2\, d\tau \\ &= \sum_r c_r^2\end{aligned} \tag{10.101}$$

since $\int \phi_r^2\, d\tau = 1$. The total electron density q_r at an atom is the sum of electron densities contributed by each electron in each M.O., so that

$$q_r = \sum_r r_j\, c_{jr}^2 \tag{10.102}$$

where c_{jr} is the coefficient of atom r in the jth M.O. It should be noted that j represents the electron related to a particular carbon atom and nj represents the number of electrons in an orbital.

The detailed calculation of charge-density for different molecules is illustrated below.

10.4.1 BUTADIENE

The two molecular orbitals of butadiene ϕ_1 and ϕ_2 given by

$$\phi_1 = 0.3717\, \chi_1 + 0.6015\, \chi_2 + 0.6015\, \chi_3 + 0.3717\, \chi_4$$
$$\phi_2 = 0.6015\, \chi_1 + 0.3717\, \chi_2 - 0.3717\, \chi_3 - 0.6015\, \chi_4$$

are occupied in the ground state by two electrons. Consequently, the total density at atom 1 will be given by

$$q_1 = 2\,(c_{11}^2 + c_{12}^2)$$

$=$ no. of electrons in an orbital × square of the coefficient of 1st atomic orbital + square of the coefficient of 1st a.o.)

so that

$$q_1 = 2\,\{(0.3717)^2 + (0.6015)^2\} = 1 \tag{10.103}$$

The charges q_2, q_3 and q_4 on the atoms 2, 3 and 4 would have the magnitude given by,

$$q_2 = 2\,(c_{21}^2 + c_{22}^2)$$
$$= 2\,(0.6015^2 + 0.3717^2) = 1 \tag{10.104}$$

$$q_3 = 2\,(c_{31}^2 + c_{32}^2)$$
$$= 2\,[(0.6015^2 + (-0.3717)^2] = 1 \tag{10.105}$$

and

$$q_4 = 2\,(c_{41}^2 + c_{42}^2)$$
$$= 2\,[0.3717^2 + (-0.6015)^2] = 1 \tag{10.106}$$

Thus, in butadiene, the electron densities of all the carbon atoms are equal to unity. This is true for all the polyenes.

10.4.2 BENZENE

In the case of benzene each of the three orbitals ϕ_1, ϕ_2 and ϕ_3, are occupied by two electrons in the ground state, therefore the electron density at carbon atom 1 is given by

$$q_1 = 2\,(c_{11}^2 + c_{12}^2 + c_3^2) \tag{10.107}$$

$$= 2\left[\left(\frac{1}{\sqrt{6}}\right)^2 + \left(\frac{2}{\sqrt{12}}\right)^2 + 0\right]$$

$$= 2\,(\tfrac{1}{6} + \tfrac{1}{3}) = 1 \tag{10.108}$$

Similarly the electron density at carbon atom 2 is given by

$$q_2 = 2\,[c_{21}^2 + c_{22}^2 + c_{23}^2] \tag{10.109}$$

$$= 2\left[\left(\frac{1}{\sqrt{6}}\right)^2 + \left(\frac{1}{\sqrt{12}}\right)^2 + \left(\frac{1}{\sqrt{4}}\right)^2\right]$$

$$= 2\,[\tfrac{1}{6} + \tfrac{1}{12} + \tfrac{1}{4}]$$

$$= 2\left[\frac{2+1+3}{12}\right] = 1 \tag{10.110}$$

and the electron density at carbon atom 3 is given by

$$q_3 = 2\,(c_{31}^2 + c_{32}^2 + c_{33}^2) \tag{10.111}$$

$$= 2\left[\left(\frac{1}{\sqrt{6}}\right)^2 + \left(\frac{1}{\sqrt{12}}\right)^2 + \left(\frac{1}{\sqrt{4}}\right)^2\right]$$

$$= 2\,[\tfrac{1}{6} + \tfrac{1}{12} + \tfrac{1}{4}]$$

$$= 1 \tag{10.112}$$

Further, we can show that

$$q_4 = q_5 = q_6 = 1 \tag{10.113}$$

Thus

$$q_1 = q_2 = q_3 = q_4 = q_5 = q_6 = 1 \tag{10.114}$$

Hence in Benzene the π-electron density at all the carbon atoms is equal to unity.

10.4.3 ETHYLENE

There are only two π-electrons in this molecule and these occupy the molecular orbital

$$\phi = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$$

The electron density at carbon 1 is, therefore given by

$$q_1 = 2\left(\frac{1}{\sqrt{2}}\right)^2 = 1 \tag{10.115}$$

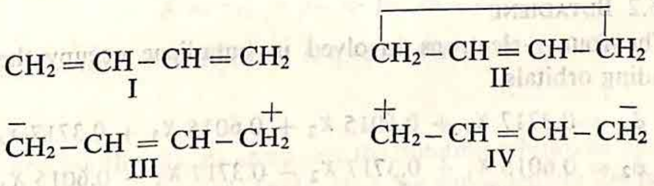
and the electron density at carbon 2 is given by

$$q_2 = 2\left(\frac{1}{\sqrt{2}}\right)^2 = 1 \tag{10.116}$$

Thus the π-electron density on the two carbon atoms of ethylene is equal to unity.

10.5. Bond Order

In classical organic chemistry the bond order has always been supposed to be an integer but new facts emerging from theoretical studies suggest the possibility of a fractional order. The end C—C bonds and the central bond of butadiene were formerly considered to have bond orders of 2 and 1 respectively. In view of quantum mechanical interpretation, butadiene can no longer be represented by structure I but structures II, III and IV must also be considered.



$CH_2=CH-CH=CH_2$ I

$CH_2-CH=CH-CH_2$ II

$\overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2$ III

$\overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2$ IV

Resonance among the above four structures imparts a certain amount of double bond character to the central bond in structure I and decreases the importance of the two double bonds at the end carbon atoms. One is therefore led to the concept of a fractional bond order. Coulson suggested that the bond order of any given bond is the sum of contributions from each of the occupied M.O.'s. The partial mobile bond order p^j_{rs} for the $r-s$ bond in the jth M.O. is defined as

$$p^j_{rs} = c_{jr}\, c_{js} \tag{10.117}$$

The total bond order is defined as

$$p_{rs} = \sum_{\text{all electrons}} p^{j}_{rj} = \sum n_j \, c_{jr} \, c_{js} \tag{10.118}$$

in which nj is the number of electrons in the jth M.O. Since the bond order is associated with the π-electrons only, we may simply call it as π-bond order.

10.5.1 EHYLENE

The partial bond order p_{12} associated with the molecular orbital $\phi_1 = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2)$ is given by

$$p^1_{12} = \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} = \tfrac{1}{2}$$

Using equation (10.117) similarly, the partial bond order associated with the anti-bonding orbital is given by

$$p^2_{12} = \frac{1}{\sqrt{2}} \left(-\frac{1}{\sqrt{2}} \right) = -\tfrac{1}{2}$$

It follows that a positive value of partial bond order strengthens the π-bond while a negative value weakens it.

Since in the ground state of ethylene, two π-electrons belong to ϕ_1, the total π-bond order $p_{12} = 2 \, p^1_{12} = 2 \cdot \frac{1}{2} = 1$.

10.5.2 BUTADIENE

The four π-electrons involved in butadiene occupy the two bonding orbitals,

$$\phi_1 = 0.3717 \, \chi_1 + 0.6015 \, \chi_2 + 0.6015 \, \chi_3 + 0.3717 \, \chi_4$$

$$\phi_2 = 0.6015 \, \chi_1 + 0.3717 \, \chi_2 - 0.3717 \, \chi_3 - 0.6015 \, \chi_4$$

Accordingly we get the following values for the partial bond orders between different carbon atoms; thus

$$p^1_{12} = 0.3717 \times 0.6015 = 0.224$$

$$p^1_{23} = 0.6015 \times 0.6015 = 0.362$$

and $$p^1_{34} = 0.6015 \times 0.3717 = 0.224$$

We see that $p^1_{23} > p^1_{12} = p^1_{34} > 0$. This shows that the contribution of the electrons belonging to ϕ_1 strengthens the central bond.

Similarly, the partial bond order, for ϕ_2 would be given by

$$p_{12}^2 = 0.6015 \times 0.3717 = 0.22358 = 0.224$$

$$p_{23}^2 = 0.3717 \times (-0.3717) = -0.138$$

$$p_{34}^2 = (-0.3717) \times (-0.6015) = 0.224$$

Thus, $p_{12}^2 > p_{34}^2 > 0 > p_{23}^2$

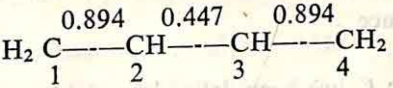
The above results show that electrons in ϕ_2 strengthens the two end bonds and not the central bonds.

Having calculated the fractional bond orders, we can calculate the π-bond orders as follows:

$$p_{12} = 2\,p_{12}^1 + 2\,p_{12}^2 = 0.894 = p_{34}$$

$$p_{23} = 2\,p_{23}^1 + 2\,p_{23}^2 = 0.447$$

where 2 stands for the number of electrons in each orbital. We can summarise the above results by the following molecular diagram.



$$\underset{1}{H_2\,C}\overset{0.894}{\text{---}}\underset{2}{CH}\overset{0.447}{\text{---}}\underset{3}{CH}\overset{0.894}{\text{---}}\underset{4}{CH_2}$$

The sum of π-bond orders is given by

$$S = p_{12} + p_{23} + p_{34} = 2.236$$

Thus, the total π-bond order is greater than two by 0.236.

Benzene

Knowing that ϕ_1, ϕ_2 and ϕ_3 are the bonding orbitals of benzene and using the results of Table 10.2, we can calculate the partial bond order and π-bond order as follows,

Fractional Bond Orders

$$p_{12}^1 = \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{6}} = \frac{1}{6}$$

$$p_{12}^2 = \frac{2}{\sqrt{12}} \cdot \frac{2}{\sqrt{12}} = \frac{1}{6}$$

$$p_{12}^3 = 0$$

$$p_{23}^{1} = \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{6}} = \tfrac{1}{6}$$

$$p_{23}^{2} = \frac{1}{\sqrt{12}} \cdot \frac{1}{\sqrt{12}} = \tfrac{1}{12}$$

$$p_{23}^{3} = \frac{1}{\sqrt{4}} \cdot \frac{1}{\sqrt{4}} = \tfrac{1}{4}$$

π-Bond Order

$$p_{12} = 2\left(\tfrac{1}{6} + \tfrac{1}{6}\right) + 0$$

$$= \tfrac{2}{3} = 0.667$$

and
$$p_{12} = p_{23} = p_{34} = p_{45}$$

$$p_{23} = 2\left(\tfrac{1}{6} - \tfrac{1}{12} + \tfrac{1}{4}\right) = \tfrac{2}{3} = .667$$

Thus,
$$p_{12} = p_{23} = p_{34} = p_{34} = p_{45}$$

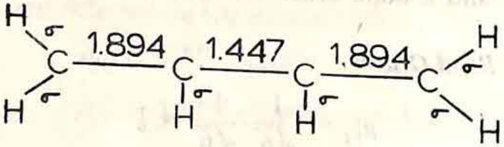
Therefore all six bonds are equivalent, as expected.

10.6. Free Valence

The free valence F_r has been defined by Coulson as

$$F_r = N_{max} - N_r$$

where N_r = sum of the orders of all bonds joining atom r and s. N_{max} = maximum value, usually taken as $\sqrt{3}$. If we assign a bond order of unity to all σ-bonds then N_r is defined as the sum of all bond orders, consequently N_r measures the total degree of bonding. We shall first illustrate how N_r is estimated in the case of butadiene for which the molecular diagram is as follows.



We have,
$$p_{12} = 1.894$$

$$p_{23} = 1.447$$

The total bond number N_1 for atom 1 is, therefore given by

$$N_1 = 1.894 + 2\times 1.0 = 3.894$$

Similarly $\quad N_2 = 1.894 + 1.447 + 1.0 = 4.341$

On account of the symmetry of the molecule

$$N_1 = N_4$$

and $\quad N_2 = N_3$

Similarly for benzene, it can be shown that

$$p_{12} = p_{16} = 0.667$$

and therefore $\quad N_1 = 1.667 + 1.667 + 1.6 = 4.334$

It is easy to show that $N_1 = N_2 = N_3 = N_4 = N_5 = N_6 = 4.33$. Thus in contrast to butadiene all N values of benzene carbon atoms are equivalent.

Moffitt (1949) has shown that for carbon

$$N = 3 + \sqrt{3} = 4.732$$

According to some authors (Coulson et al. 1951) this value of N_{max} is true only for tertiary carbon atoms (e.g., 9 and 10 positions of naphthalene). For a secondary carbon atom

$$N_{max} = 3 + \sqrt{2} = 4.414$$

and for a primary carbon atom

$$N_{max} = 3 + \sqrt{1} = 4.000$$

In the calculations that follow, we shall assume, following Greenwood, that $N_{max} = 4.732$.

Thus, $\quad F_r = N_{max} - N_r = 4.732 - N_r$

Thus, for butadiene

$$F_1 = F_4 = 4.732 - 3.894 = .838$$

and $\quad F_2 = F_3 = 4.732 - 4.341 = 0.391$

Similarly for benzene

$$F_1 = F_2 = \ldots F_6 = 4.732 - 4.334 = 0.398$$

10.7. Molecular Orbital Treatment of Naphthalene

M.O. calculations on naphthalene (Fig. 10.5) using the atomic orbital basis set would involve solving a 10×10 secular determinant and evaluating ten 9×9 minors to calculate the coefficients. We can greatly reduce the amount of work needed for the π-electron calculation on naphthalene by making use of the fact that naphthalene has three symmetry operations that leave the molecule indistinguishable from its original configuration. These symmetry operators are two mirror planes σ_v, σ_v' and a two-fold axis of rotational symmetry, c_2.

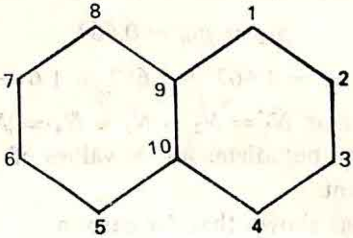


Fig. 10.5. Naphthalene.

The plane of the molecule is also a reflection plane, but all orbitals must have eigenvalve with negative sign with respect to reflection in this plane. Hence its use does non result in any simplification of the problem. The ten $2p-$carbon orbitals perpendicular to the plane of naphthalene molecule interact to form π-orbitals. Since the molecule is not a regular polygon and that it has no central atom present, the molecular orbitals cannot be found directly. Naphthalene belongs to the *Symmetry group* D_{2h} and it is obvious that the operations of this group make following atoms equivalent,

(a) 2, 3, 6, 7; (b) 1, 4, 5, 8; (c) 9, 10,

The molecular orbitals of these three sub-groups can be found and then allowed to interact to form the π-orbitals of naphthalene. The coefficients for each orbital in a sub-group have the same magnitude but they differ in sign.

Since $c_2 = \sigma_2 \times \sigma_v'$ it is obvious that all operations cannot have eigenvalue $-1, -1, -1$. Symmetry orbitals can now be constructed by taking the atomic orbitals one at a time, performing the operations $E, c_2, \sigma_v, \sigma_v'$. For example, if we take χ_1 and the set of eigenvalues A_1, we can obtain the symmetry orbital as follows

$$\chi_1(A) = \chi_1 + \chi_5 + \chi_8 + \chi_4$$

since

$$E\chi_1 = \chi_1$$

$$c_2\,\chi_1 = \chi_5$$

$$\sigma_v\,\chi_1 = \chi_8$$

$$\sigma_v'\,\chi_1 = \chi_4$$

Likewise, a symmetry orbital with a B_1 set of eigenvalues formed from atomic orbital χ_2 would be given by

$$\chi_2\,(B_1) = \chi_2 - \chi_6 - \chi_3 + \chi_7$$

By using this procedure, using different atoms with each set of eigenvalues, one can construct the set of 10 symmetry orbitals given in Table 10.3.

Table 10.3. Symmetry orbitals for naphthalene

A_1	A_2
$S_1 = \frac{1}{2}(\chi_1 + \chi_4 + \chi_5 + \chi_8)$	$S_4 = \frac{1}{2}(\chi_1 - \chi_7 + \chi_5 - \chi\ )$
$S_2 = \frac{1}{2}(\chi_1 + \chi_3 + \chi_6 + \chi_7)$	$S_5 = \frac{1}{2}(\chi_2 - \chi_3 + \chi_6 - \chi_7)$
$S_3 = \frac{1}{2}(\chi_9 + \chi_{10})$	
B_1	B_2
$S_6 = \frac{1}{2}(\chi_1 - \chi_4 - \chi_5 + \chi_8)$	$S_9 = \frac{1}{2}(\chi_1 + \chi_4 - \chi_5 - \chi_8)$
$S_7 = \frac{1}{2}(\chi_2 - \chi_3 - \chi_6 + \chi_7)$	$S_{10} = \frac{1}{2}(\chi_2 + \chi_3 - \chi_6 - \chi_7)$
$S_8 = \frac{1}{\sqrt{2}}(\chi_9 - \chi_{10})$	

From M.O. theory, when we put $x = \dfrac{\alpha - E}{\beta}$

We have,

$$x\,c_\mu + \sum_{\nu \to \mu} c_\nu = 0 \qquad (10.119)$$

The secular equations for atoms, 1, 2 and 9 are

$$\begin{aligned} x\,c_1 + c_2 + c_9 &= 0 \\ c_1 + (x+1)\,c_2 &= 0 \qquad (10.120) \\ 2c_1 + (x+1)\,c_9 &= 0 \end{aligned}$$

which yields

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x+1 & 0 \\ 2 & 0 & x+1 \end{vmatrix} = 0 \qquad (10.121)$$

On solving we get

$$(x+1)(x^2 + x - 3) = 0 \qquad (10.122)$$

So that, $\quad x = 1.303, -1, -2.303$

Putting $x = 1$ in equation (10.120), we find,

$$c_1 = 0; c_2 = c_9 \qquad (10.123)$$

Similarly, we can show that

$$c_4 = c_5 = c_8 = 0 \qquad (10.124)$$

$$c_3 = c_6 = c_7 = c_8 = c_2 \qquad (10.125)$$

and
$$c_9 = c_{10} \qquad (10.126)$$

Coefficients of bonding orbitals of naphthalene and Hückel energies are given in Table 10.4.

Table 10.4. Coefficients of bonding orbitals

c_1	c_2	c_9	$x = (\alpha - E)/\beta$
0.4253	0.2629	0	−0.618
0	0·4082	−0.4082	−1.000
0.3996	0.1733	0.3470	−1.303
0.2628	0.4253	0	−1.618
0.3006	0.2307	0.4614	−2.303

Quantum mechanical treatment of large organic molecules has been illustrated in this chapter. The spectroscopic properties of such molecules can be predicted on the basis of the knowledge of energy levels. These can also be used for calculating delocalisation energy. Electron density calculations can be used to predict reactivity at specific centres in the molecule. For example an electrophile would get attached to the carbon atom where electron density is highest. Further, the strength of the bonds in an organic molecule can be assessed on the basis of bond order and free valence.

Electron density contour maps can also be drawn by making use of X-ray diffraction data of single crystals. From X-ray data, structure factors can be evaluated, the Fourier transform of which yields electron density. Thus from X-ray data electron density can be calculated around the nuclei in the molecule and a picture of electron cloud can be obtained which is represented by a contour diagram. A typical contour diagram of maleic acid is shown in Fig. 10.6. In a similar manner, neutron density contours for benzene have been determined by neutron diffraction method

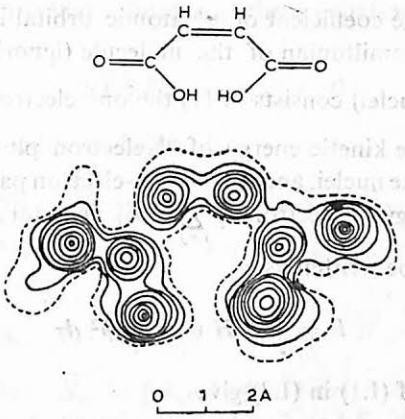


Fig. 10.6. Electron density contour diagram of crystalline maleic acid.

(C.A. Coulson, *The Shape and Structure of Molecules*, Oxford University Series, Clarendon Press, p. 2-3, 1973).

In recent years, the experimental electron density diagrams have been used for the verification of quantum mechanical theories of large molecules based on different approximations.

APPENDIX 1: APPROXIMATE METHODS IN M.O. THEORY OF LARGE MOLECULES

In molecular orbital theory, the molecular wave function of a closed shell molecule is written as a product (Hartree approach) or a determinant (Hartree-Fock approach) involving all molecular orbitals. The molecular wave function in latter approach is anti-symmetric to exchange of any two electrons and thus satisfies the Pauli exclusion principle, whereas it does not do so in Hartree approach. All important principles, however, can be illustrated by employing a Hartree product of n molecular orbitals as molecular wave function,

$$\psi\,(1, 2, \ldots .\, n) = \psi_1\,(1)\,\psi_2\,(2) \ldots .\, \psi_n\,(n) \qquad \text{(I.1)}$$

The molecular orbitals ψ_i are assumed to be orthonormal and are expressed as linear combinations of atomic orbitals ϕ_μ

$$\psi_i = \sum_{\mu=1}^{n} C_{i\mu}\,\phi_\mu \qquad \text{(I.2)}$$

where $C_{i\mu}$ is the coefficient of μ^{th} atomic orbital in i^{th} molecular orbital. The Hamiltonian of the molecule (ignoring the mutual repulsion of nuclei) consists of (1) the one-electron part $\sum_{i=1}^{n} H(i)$, where $H(i)$ the kinetic energy of i^{th}-electron plus its attraction energy to all the nuclei, and (2) the two-electron part—the mutual repulsion energy of electrons $\frac{1}{2}\sum_{i\neq j} e^2/r_{ij}$. The total energy of the molecule can be written as

$$E = \int \psi\, H\, \psi\, d\tau \int \psi^2\, d\tau \tag{I.3}$$

Substitution of (I.1) in (I.3) gives

$$E = \int \psi_i\,(i)\, H\,(i)\, \psi_i\,(i)\, d\tau_l + \sum_{i<j} \int \psi_i\,(i)\, \psi_j\,(j)\, \frac{e^2}{r_{ij}}\, \psi_i \times (i)\, \psi_j\,(j)\, d\tau_l\, d\tau_j \tag{I.4}$$

Substituting (I.2) in (I.4) we obtain

$$E = \sum_i \sum_\mu \sum_\nu C_{i\mu}\, C_{i\nu}\, H_{\mu\nu} + \sum_{i<j} \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma \times C_{i\mu}\, C_{j\lambda}\, C_{i\nu}\, C_{j\sigma}\, (\mu\nu/\lambda\sigma) \tag{I.5}$$

where

$$H_{\mu\nu} = \int \phi_\mu\,(i)\, H\,(i)\quad \phi_\nu\,(i)\, d\tau_i \tag{I.6}$$

and

$$(\mu\nu/\lambda\sigma) = \int \phi_\mu\,(i)\, \phi_\lambda\,(j)\, \frac{e^2}{r_{ij}}\, \phi_\nu\,(i)\, \phi_\sigma\,(j)\, d\tau_i\, d\tau_j \tag{I.7}$$

are one and two-electron integrals respectively. Whereas $H_{\mu\nu}$ could be a one-, two- or a three-centre integral, the electron repulsion integral $(\mu\nu/\lambda\sigma)$ could be a one-, two-, three- or four-centre integral. In (I.5), three- and four-centre integrals are fairly difficult to compute.

The energy E in (I.5) is now minimised with respect to the variation of coefficients $C_{i\mu}$ $(i, \mu = 1, 2, \ldots n)$ subject to the constraint that the resulting molecular orbitals are orthonormal. This procedure results in a set of equations

$$\sum_\nu (F_{\mu\nu} - \epsilon_\mu\, S_{\mu\nu})\, c_{\mu\nu} = 0 \qquad (\mu, \nu = 1, \ldots n) \tag{I.8}$$

The only non-trivial solutions of these equations are those for which

$$\det \mid F_{\mu\nu} - \epsilon_{\mu} S_{\mu\nu} \mid = 0 \tag{I.9}$$

which is expanded form looks like

$$\left.\begin{array}{llll} F_{11}-\epsilon_1 S_{11} & \epsilon_{12}-\epsilon_1 S_{12} & F_{13}-\epsilon_1 S_{13} & F_{1n}-\epsilon_1 S_{1n} \\ F_{21}-\epsilon_2 S_{21} & F_{22}-\epsilon_2 S_{22} & F_{23}-\epsilon_2 S_{23} \ldots & F_{2n}-\epsilon_2 S_{2n} \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ F_{n1}-\epsilon_n S_{n1} & F_{n2}-\epsilon_2 S_{n2} & \cdots\cdots & F_{nn}-\epsilon_n S_{nn} \end{array}\right| \tag{I.10}$$

In these equations $S_{\mu\nu} = \int \phi_{\mu}(1)\, \phi_{\nu}(1)\, d\tau_1$ is overlap integral. ϵ_{μ} is the energy of μ^{th} molecular orbitals and $F_{\mu\nu}$ are the elements of so-called Fock matrix and are given by

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{j=1}^{occ} \sum_{\lambda} \sum_{\sigma} n_j\, c_{j\lambda}\, c_{j\sigma}\, (\mu\nu/\lambda\sigma) \tag{I.11}$$

where *occ* denotes the number of occupied orbitals, n_j being the number of electrons in j^{th} molecular orbital. Since elements $F_{\mu\nu}$ depends on the unknown coefficients $c_{j\lambda}$, they are evaluated iteratively. One first assumes certain values for coefficients $c_{j\lambda}$, computes all $F_{\mu\nu}$ and solves (I.10). This gives a set of molecular orbital energies ϵ_{μ} and computed coefficients $c_{j\lambda}$. This new set of coefficients is again used to compute new $F_{\mu\nu}$ from (I.11), which in turn yield new ϵ_{μ} and $c_{j\lambda}$ from (I.10). This procedure is repeated several times, till the coefficients $c_{j\lambda}$ in two successive interactions have converged within a prespecified tolerance. If instead of Hartree product function (I.1), the determinantal wave function is used (I.11) is modified to

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{j=1}^{occ} \sum_{\lambda} \sum_{\sigma} n_j\, c_{j\lambda}\, c_{j\sigma}\, (\mu\nu/\lambda\sigma) - \tfrac{1}{2}\, (\mu\nu/\nu\sigma) \tag{I.12}$$

Rest of the procedure and equations for evaluation of molecular orbital energies still remains same.

For each element $F_{\mu\nu}$, one has to compute n^2 one-electron integrals and n^4 two electron integrals, all of which are evaluated exactly in *ab initio* computation. For example, in a 100-orbital molecule, one has to compute 10,000 one-electron and 100 million two-electron integrals and this poses a tremendous computational and storage problems even for largest and fastest computers. In any case, these computations are very costly and time consuming and their use is restricted only to small molecule.

Most of the approximate methods try to reduce the number of these n^4 integrals to something like n^3 or n^2 integrals by some trick or parameterisation procedure. The product, $\phi_\mu (1) \phi_\nu (1)$ is called the differential overlap. For $\mu \neq \nu$, if $\phi_\mu (1) \phi_\nu (1)$ is consistently neglected in all electron repulsion integrals (that is retaining only n^2 integrals of the type $(\mu\mu/\lambda\lambda)$, we have the so-called CNDO (complete neglect of differential overlap) approximation or one of its variants. On the other hand if the differential overlap is neglected everywhere, except in one-centre integral we have INDO (intermediate neglect of differential overlap) approximation. If $\phi_\mu (1) \phi_\nu (1)$ is neglected only if ϕ_μ and ϕ_ν are atomic orbitals centred on different nuclei, we have so-called NDDO (neglect of diatomic differential overlap) approximation. Likewise there are several variants of these ZDO methods, depending upon how many integrals are neglected and how rest of them are evaluated. Even under these approximations, sometimes only valence orbitals are considered in M.O. calculations. These methods include CNDO, INDO, MINDO etc. Sometimes all σ-electrons are ignored and only π-electrons are considered explicitly. When all two electron integrals surviving after ZDO approximation are computed by certain parameterisation procedures, we have the PPP (Pople-Pasiu-Parr) approximation. In EXT (extended Hückel Theory) all two electron integrals are ignored, whereas in simple Hückel approach even overlap integrals are neglected. The surviving one-electron integrals are parameterised and thus in this method, not a single integral is evaluated.

Various Approximate M.O. methods used in Quantum Mechanical calculations are listed below:

A. All electron calculation
   VRDDO, MODPOT, PRDDO, PCILO etc.

B. Valence Electron Calculation
   CNDO, INDO, MINDO, NNDO, SPINDO, EHT, IEHT

C. π-electron calculations
   FEMO
   PPP
   SHT

APPENDIX II: GENERALISED TREATMENT OF SIMPLE HÜCKEL MOLECULAR ORBITAL THEORY (SHMO)

For large molecules containing π-electron, approximate method developed by E. Hückel has been quite popular. The following approximations are made in Hückel method.

i) σ-bonds are assumed to be localised.

ii) Interaction between σ- and π-electrons is neglected, i.e. the Hamiltonian H is considered to be the sum of the Hamiltonian of σ-electrons and π-electrons.

$$H = H_\alpha + H_\pi \tag{II.1}$$

and

$$E = E_\alpha + E_\pi \tag{II.2}$$

$$\psi = \psi_\alpha \cdot \psi_\pi \tag{II.3}$$

where E is the energy and ψ the wave function. The subscript indicate the σ- and π-electron contribution.

iii) Interelectronic repulsion is neglected.

iv) $H_{ij} = 0$ for nonadjacent atoms which are not bonded together.

v) $S_{ii} = 1$ and $S_{ij} = 0$ for nonadjacent atoms $(i \neq j)$.

$S_{ij} = \int \phi_i \, \phi_j d\tau$ is called an overlap integral, since it is a measure of the overlap of ith and jth orbitals. Let us discuss the character of H_{ii}, H_{ij}, S_{ii} and S_{ij} in a little greater detail.

S_{ij} depends on the internuclear distance r_{ij}. The calculations made by Mulliken are plotted in Fig. II.1, which show their interdependence. However, when $S_{ij} = 0$ $(i \neq j)$, it considerably simplifies the calculation. (Roberts, J.D., Notes on Molecular Orbital) Calculations, Benjamin, New York (1962).

The resonance integral $H_{ij} = \int \phi_i \, H \phi_j \, d\tau$ when $i \neq j = \beta_{ij}$,

β_{ij} is a function of atomic number, orbital types and degree of overlap. It is also a function of the internuclear distance. Calculations made by Mulliken are shown in Fig. II.2 which shows how β_{ij} depends on r_{ij} for carbon 2 p-π overlap relative to that of isolated carbon.

From Fig. II.2 it follows that as r_{ij} increases β_{ij} decreases. Hence it is not a bad approximation to put $\beta_{ij} = 0$ when i and j are not nearest neighbours.

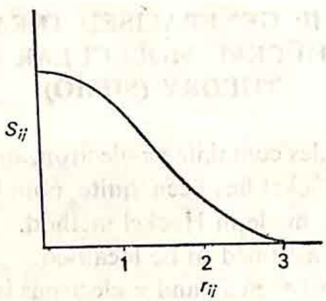


Fig. II.1. Interdependence of S_{ij} and r_{ij}.

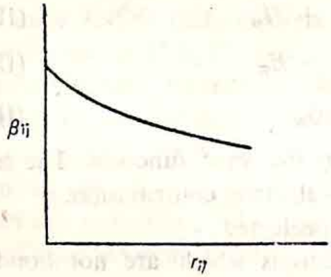


Fig. II.2. Dependence of B_{ij} or r_{ij}.

The Coulomb integral $H_{ii} = \int \phi_i \, H \, \phi_i \, d\tau = \alpha$, where α is a function of nuclear charge. α is clearly a negative number.

We can devide the organic molecules containing π-electrons into two categories (a) open chain and conjugated π-electron systems (b) cyclic π-electron systems like C_6H_6. We discuss below how HMO method can be applied to both these types.

a) Open chain and conjugated π-electron systems:

For open chain π-electron molecules, containing n_π number of π-electrons, yield this following determinants, having n_π-rows and n_π-columns.

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \; \ldots & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \; \ldots & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta \; \ldots & 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots , \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & 0 \; \ldots & \beta & \alpha - E & \beta \\ 0 & 0 & 0 & 0 \; \ldots & 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad \text{(II.4)}$$

Now if we put $x = \dfrac{\alpha - E}{\beta}$, then equation (II.4) takes the form

$$\begin{vmatrix} \chi & 1 & 0 & & \cdots & 0 & 0 & 0 \\ 1 & \chi & 1 & & \cdots & 0 & 0 & 0 \\ 0 & 1 & \chi & 1 & \cdots & 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & & \cdots & 1 & \chi & 1 \\ 0 & 0 & 0 & & \cdots & 0 & 1 & \chi \end{vmatrix} = 0 \tag{II.5}$$

The general solutions for above determinant is

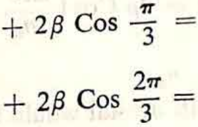
$$\chi = -2\,\mathrm{Cos}\left(\frac{k\pi}{n_\pi + 1}\right) \tag{II.6}$$

where $k = 1, 2, 3, \ldots, n_\pi$ and n_π is the number of π-electrons in a molecule. Thus the energy of the kth orbital would be

$$E_k = \alpha + 2\beta\,\mathrm{Cos}\left(\frac{k\pi}{n_\pi + 1}\right)$$

Since β is negative, E_1 will be the lowest energy orbital.

EXAMPLE: For ethylene molecule, $n_\pi = 2$

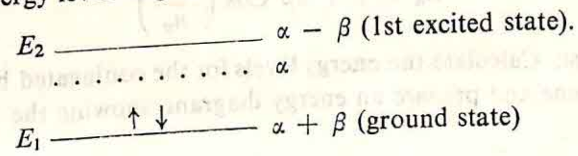


Therefore,

$$E_1 = \lambda + 2\beta\,\mathrm{Cos}\,\frac{\pi}{3} = \alpha + \beta \tag{II.7}$$

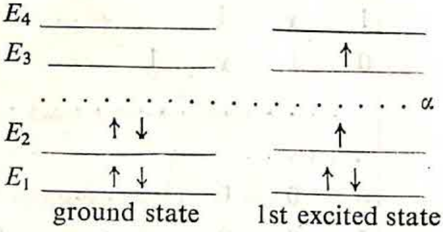
$$E_2 = \alpha + 2\beta\,\mathrm{Cos}\,\frac{2\pi}{3} = \alpha - \beta \tag{II.8}$$

The energy level diagram can be represented as follows


E_2
$\alpha - \beta$ (1st excited state).
α
↑↓
E_1
$\alpha + \beta$ (ground state)

Problem: Calculate the energy levels for the conjugate bonding in 1, 3-butadiene. Draw this energy diagram showing this ground and this first excited state.

$E_1 = \alpha + 1.618\beta$
$E_2 = \alpha + 0.618\beta$
$E_3 = \alpha - 0.618\beta$
$E_4 = \alpha - 1.618\beta$



b) Simple Hückel molecular orbital (HMO) theory of cyclic compounds:

For cyclic organic compounds containing π-electrons, a secular determinant (II.4), using HMO as in case of open chain molecules, can be written as:

$$\begin{vmatrix} x & 1 & 0 & 0 & \ldots & 0 & 0 & 1 \\ 1 & x & 1 & 0 & \ldots & 0 & 0 & 0 \\ 0 & 1 & x & 1 & \ldots & 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & 0 & \ldots & 1 & x & 1 \\ 1 & 0 & 0 & 0 & \ldots & 0 & 1 & x \end{vmatrix} = 0 \qquad \text{(II.9)}$$

The general solution for equation (II.9) can be written as

$$x = 2p \operatorname{Cos}\left(\frac{2k\pi}{n_\pi}\right)$$

where $k = 0, 1, 2, \ldots . n_\pi$
and the energy of the kth orbital would be.

$$E_k = \alpha + 2\beta \operatorname{Cos}\left(\frac{2k\pi}{n_\pi}\right)$$

Problem: Calculate the energy levels for the conjugated bonding in Benzene and prepare an energy diagram, showing the ground state.

For,

$$k = 1, \quad E_1 = \alpha + 2\beta \cos(\pi/3) = \alpha + \beta$$

$$k = 2, \quad E_2 = \alpha + 2\beta \cos(2\pi/3) = \alpha - \beta$$

$$k = 3, \quad E_3 = \alpha + 2\beta \cos(3\pi/3) = \alpha - 2\beta$$

$$k = 4, \quad E_4 = \alpha + 2\beta \cos(4\pi/3) = \alpha - \beta$$

$$k = 5, \quad E_5 = \alpha + 2\beta \cos(5\pi/3) = \alpha + \beta$$

$$k = 6, \quad E_6 = \alpha + 2\beta \cos(6\pi/3) = \alpha + 2\beta$$

CHAPTER 11

Complex Inorganic Compounds

A complex ion is a charged aggregate which is formed when a metal atom or ion is directly attached to a group of neutral molecules or ions. The former is called the central ion or acceptor while the latter are called ligands or donor groups. The ligand atoms are arranged in a definite geometry. The number of such ligands bonded to the central ion is called the coordination number of that ion in the first coordination sphere. A typical example of complex ion is [Cu $(H_2O)_4^{2+}$]. Typical examples of the complex compound are Fe $(CO)_5$ and [Co $(NH_3)_3$ $(NO_2)_3$].

The explanation of bonding in such compounds would be discussed in this chapter. The stereochemistry, electronic spectra, isomerism and magnetic properties of such complexes have been investigated during recent years. A satisfactory theory of bonding must give an adequate explanation of all these. Two things have been clearly established by experiments. The central ion is the metal ion and *d*-electrons of the ion are involved in bonding. Werner in 1893 postulated the existence of secondary or nonionisable valencies. On the basis of his researches on a very large number of complex compounds, Werner was able to elucidate the number, nature and spatial arrangement of these valencies. However, there was no theoretical justification for these types of valencies. With the development of electronic theory, a self-consistent explanation of the types of valencies in terms of electrovalency and covalency could be obtained. Sidgwick gave the concept of effective atomic number (EAN) based on the concept of coordinate bond which put the above ideas on still sounder footing.

The above classical coordination theory does not explain the mechanism of bonding the ligands to the central ion and consequently cannot explain the spectral and magnetic properties. With this objective following theories have been proposed:

i) Electrostatic theory with its more recent crystal field modifications,

ii) Valence bond theory,

iii) Molecular orbital theory, and

iv) Ligand field theory which is a combination of (i) and (iii).

11.1 Electrostatic Theory

The electrostatic theory is based on the assumption that the bonding of the components of the complex is determined by purely electrostatic forces. The central ion and ligands are considered to be rigid, sphere whose radius is well-defined. The stability of the complex ion can then be understood in terms of interactions between dipoles and point charges, point dipoles or combined charges all supposed to be lying at the centre of these classical spheres. Using this model, it is possible to express the heats of formation of the complexes as a function of charge, dipole moment and radius. However, the model cannot explain the existence of anomalous coordination types on a purely energetic basis. The existence of certain low-spin complexes e.g. diamagnetic cobalt (III) could however be explained on this model.

11.2 Crystal Field Theory

A modified picture is proposed in the crystal field theory where it is assumed that the orbitals of the central ion are separated from the ligand orbitals. The theory takes into account the influence of the various possible electrostatic fields which arise due to different geometries and strengths of various ligands on the five *d*-orbitals of a transition metal ion. It is to be noted that the basis of the theory is that the degeneracy of the *d*-orbitals on the central atom is removed as the ligands are placed on the molecule.

11.3 Valence Bond Theory

1) The central atom provides a number of orbitals equal to its coordination number for the formation of covalent bonds with ligand orbitals.

2) The overlap of a vacant metal orbital and a filled orbital of the donor group leads to the formation of a covalent σ-bond which is simply a coordinate link.

3) The possibility of π-bond involving *d*-orbitals exists under suitable circumstances. The strength of covalent bond depends on the extent of overlap of the electron clouds according to this picture. The valence bond theory involves the hybridisation of the original atomic orbitals to form a new set of equivalent bonding orbitals having definite directional properties. The theory easily predicts the shapes and magnetic moments of complexes and the results are in agreement with experiment. The theory is simple and straightforward in application but it suffers from following defects:

1) It provides only qualitative explanations,
2) It cannot explain the spectra of complexes, and
3) It cannot predict the detailed magnetic properties.

11.4 M.O. Treatment of Complex Ions

The procedure for the M.O. treatment of complex ion is similar to that outlined in Chapter 8. The M.O.'s are generated through suitable linear combinations of the orbitals of the central ion and the orbitals of the ligand. σ, π-orbitals are obtained depending on the orientations of the latter with respect to the line-of-central ligand-central ion. σ-orbitals have rotational symmetry with respect to the direction of the bond. For π-orbitals, the bond axis contains the nodal plane. The number of M.O.'s is equal to the total number of A.O.'s under consideration. Half of these molecular orbitals are bonding orbitals. The remaining half are antibonding since the energies of these are higher than A.O.'s.

Let us try to understand bonding in an octahedral complex ion in terms of molecular orbital theory. It is commonly accepted that five *d*-orbitals of the central metal ion are essentially involved in bonding. We consider the three *p*-orbitals from each ligand, one of which has an angular function in the bond direction (σ-bond) and the other two are the perpendicular *p*-orbitals (π-bonds).

The molecular orbitals are written after the cumulative σ- and π-ligand orbitals have been spotted. The net ligand orbitals are obtained by the linear combination of orbitals of the individual ligands keeping in view the symmetry requirements. In order to write the above, let us consider Fig. 11.1 which shows the individual ligands which have to be combined for writing σ- and π-ligand orbitals in an octahedral complex ion. The resulting σ- and π-ligand orbitals are summarised in Table 11.1. The molecular orbitals can now be written by combining the orbitals of the central ion and ligand orbitals. The energy of the orbitals can then be found in the usual manner. It should be noted that M.O. method is quite tedious since sometime it needs the solution of a 30 × 30 secular determinants. But the problem can be simplified by using group theory. One simply requires to combine ligand and metal orbitals which belong to same irreducible representation.

The advantages of molecular orbital theory of bonding in complexes are as follows:

a) Experimental evidence shows that *d*-electrons of the metal ion are often delocalised on the ligands. M.O. theory best explains how this occurs.

b) M.O. theory is more useful in understanding the spectra of complexes since the excited states are more accurately described by M.O.

c) M.O.'s can be qualitatively constructed conveniently. In spite of these advantages molecular orbital theory is cumbersome

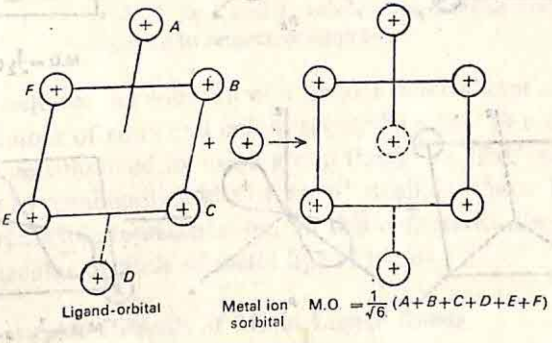
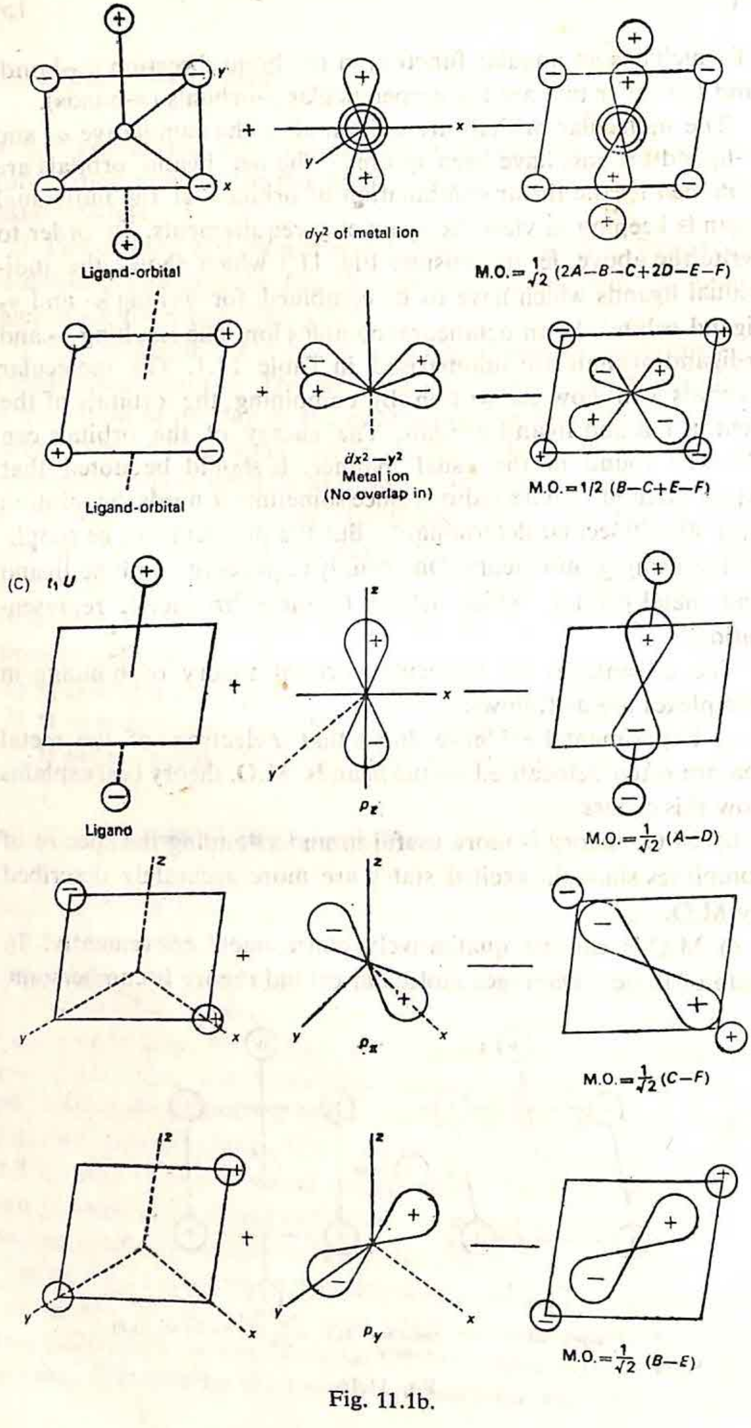


Fig. 11.1a.



Ligand-orbital
dy² of metal ion
M.O.= 1/√2 (2A−B−C+2D−E−F)
Ligand-orbital
dx²−y²
Metal ion
(No overlap in)
M.O.=1/2 (B−C+E−F)
(C) t₁U
Ligand
p_z
M.O.= 1/√2 (A−D)
p_x
M.O.= 1/√2 (C−F)
p_y
M.O.= 1/√2 (B−E)
x
y
z
+
−

Fig. 11.1b.

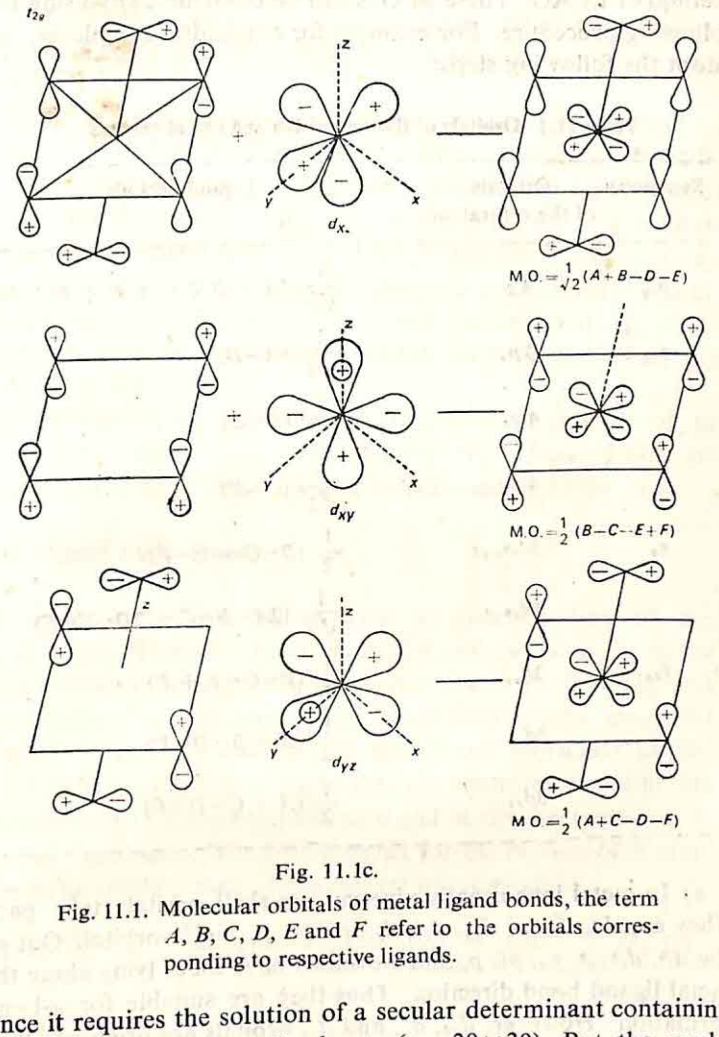

t2g
z
x
y
dx.
M.O. = 1/√2 (A + B − D − E)
z
x
y
dxy
M.O. = 1/2 (B − C − E + F)
z
x
y
dyz
M.O. = 1/2 (A + C − D − F)

Fig. 11.1c.

Fig. 11.1. Molecular orbitals of metal ligand bonds, the term *A*, *B*, *C*, *D*, *E* and *F* refer to the orbitals corresponding to respective ligands.

since it requires the solution of a secular determinant containing large number of rows and columns (say 30 × 30). But the problem can be simplified by using group theory so that one simply requires to combine ligand and metal orbitals which belong to same irreducible representation. In this context we discuss below this molecular orbitals of metal ligand bonds.

11.5 Molecular Orbitals of Metal Ligand Bonds

Molecular orbitals of metal ligand bonds are obtained by the method of LCAO. These M.O.'s can be constructed by using the following procedure. For example for octahedral complexes, we adopt the following steps:

Table 11.1. Orbitals of the central ion and ligand orbitals

Symmetry	Orbitals of the central ion	Ligand orbitals
a_{1g}	$4s$	$\frac{1}{\sqrt{6}}(A+B+C+D+E+F)$
t_{1u}	$4p_x$	$\frac{1}{\sqrt{2}}(A-D)$
	$4p_y$	$\frac{1}{\sqrt{2}}(B-E)$
	$4p_z$	$\frac{1}{\sqrt{2}}(C-F)$
e_g	$3d_{x^2-y^2}$	$\frac{1}{2}(B-C+E-F)$
	$3d_{z^2}$	$\frac{1}{\sqrt{2}}(2A-B-C+2D-E-F)$
t_{2g}	$3d_{xy}$	$\frac{1}{2}(B-C-E+F)$
	$3d_{xz}$	$\frac{1}{2}(A+B-D-E)$
	$3d_{yz}$	$\frac{1}{2}(A+C-D-F)$

a) In metal ions usually nine valence shell orbitals take part. They are d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{yz}, d_{zx}, p_x, p_y, p_z and s-orbital. Out of the d_{z^2}, $d_{x^2-y^2}$, p_x, p_y, p_z and s-orbitals have lobes lying along the metal ligand bond direction. Thus they are suitable for σ-bond formation. However, d_{xy}, d_{yz} and d_{zx} orbitals are oriented along planes and are suitable for π-bonding.

b) If a ligand possesses six σ-orbitals, the individual σ-orbital must effectively overlap with any of the six valence shell orbital, suitable for a σ-bond. They overlap with matching symmetry orbital. A positive (+) lobe of central metal ion overlaps with the positive (+) lobe of ligand orbital and similarly a negative (−) lobe of central metal ion overlaps with the negative (−) lobe of the ligand orbital.

c) If a ligand possesses a π-orbital, these orbital also combine with the metal ion orbitals suitable for π-bonding having the same symmetry.

d) Six σ-symmetry orbitals transform to a set of a_{1g}, and t_{1u} (symmetry symbols for the bonding orbitals). σ-bonds formed by s-orbital overlap of the metal ion with matching symmetry ligands orbitals are designated by a_{1g}, e_g, represents a part of d orbitals which are equivalent except for their orientation in space i.e. d_{z^2} and $d_{x^2-y^2}$ metal ion orbitals. t_{1u} represents a set of three p orbitals which are equivalent except for their orientation. t_{2g} represents a set of three equivalent d orbitals suitable for π-bonding but not for σ-bonding.

e) Each metal ion orbital can overlap with the orbitals of the ligand system which have a similar symmetry. These M.O.'s are pictorially shown in Fig. 11.1 and summarised in Table 11.1.

11.6 Ligand Field Theory

The molecular orbital theory gives an interpretation of the spectral data. However, it cannot satisfactorily account for (i) the number of absorption bands, (ii) relative location of bands, and (iii) splitting of energy levels. The ligand field theory combines the good features of electrostatic theory and molecular orbital theory. The assumption is made that the electrons move in the potential field of the central ion core and in the electrostatic potential of the ligands. The Hamiltonian for the motion of N electrons in an unfilled shell of the central ion is given by

$$H = \sum_{i=1}^{N}\left[-\frac{h^2}{\delta\pi^2 m}\Delta_i^2 - \frac{Z^*e^2}{r_i}\right] + \frac{1}{2}\sum_{i\neq j}^{N} V(\vec{r_{ij}}) + \sum_{i=1}^{N} H_{so}(i) \tag{11.1}$$

where

$-Z^* e^2/r_i =$ the potential energy of the ith electron in the field of the central ion core, where Z^* is the effective charge of the core and r_i is the distance between the central ion nucleus and the ith electron.

$V(\vec{r_{ij}}) =$ the energy of the coulomb interaction between the ith and jth electron of all ligands.

$H_{so}(\nu) =$ spin-orbit coupling energy of the ith electron.

Following three cases have to be distinguished.

a) The weak crystalline field case

$$\tfrac{1}{2}\sum_{i\neq j}\sum \frac{e^2}{r_{ij}} > \sum_{i\neq j} V(\vec{r}_{ij}) > \sum_i H_{so}(i) \tag{11.2}$$

b) The strong crystalline field case

$$\sum_{i\neq j} V(\vec{r}_{ij}) > \tfrac{1}{2}\sum_{i\neq j}\sum \frac{e^2}{r_{ij}} > \sum_i H_{so}(i) \tag{11.3}$$

c) The strong spin-orbit coupling case

$$\sum_i H_{so}(i) > \sum_{i\neq j} V(\vec{r}_{ij}),\ \tfrac{1}{2}\sum_{i\neq j}\sum \frac{e^2}{r_{ij}} \tag{11.4}$$

Like the Schrödinger equation of the free atoms or atomic ions with many electrons we cannot solve equation exactly. Accordingly efforts have been made to obtain approximate solutions. We shall, therefore, discuss ligand field theory from a qualitative angle in the following paragraphs.

We consider a case for the central cation surrounded by six ligands, at the apices of an octahedron. When the ligands are identical the actual shaps and structure of the ligand may be ignored and we may consider only the orbitals directed towards the metal ion. The set of ligand orbitals have symmetry O_h.

It can be shown by the transformation of matrices that $d_{x^2-y^2}$ and d_{z^2} belong to representation e_g and d_{xy}, d_{yz}, d_{xz} belong to t_{2g}. The ligand orbitals will interact with s, p and d_{z^2}, $d_{x^2-y^2}$ orbitals but not with d_{xy}, d_{xz}, d_{yz}.

We propose to consider the manner in which the symmetry of the chemical surrounding of an ion determines the effect of the environment of the energy levels of the ion. In the crystal field

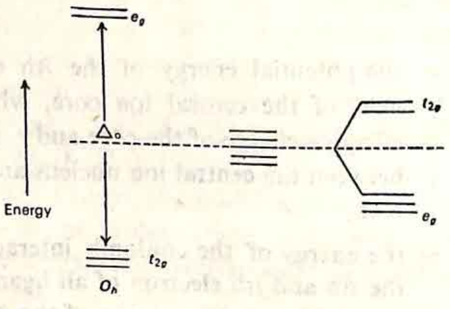


Fig. 11.2. Splitting of orbitals of O_h symmetry.

and ligand field theories, we wish to regard the effect of the environment as a small perturbation on the states of the free ion.

We may use all of the five d wave functions as a basis for a representation of the point group of a particular environment and thus determine the manner in which the set of d orbitals is split by the environment. Let us choose an octahedral environment for our first illustration. In order to determine the representation for which the set of d wave functions form a basis, we must first find the elements of the matrices which express the effect upon the set of wave functions of each of the symmetry operations in the group; the characters of these matrices will then be the characters of the representation we are seeking.

Although the full symmetry of the octahedron is O_h, we can gain all required information about the d orbitals by using only the pure rotational subgroup O because O_h may be obtained from O by adding the inversion, i. However, we already know that d orbitals are even to inversion, so that it is only the pure rotational operations of O which can bring us new information.

We assume that the wave functions of a set of d orbitals are of the general form

$$\psi = f_1(r) \cdot f_2(\theta) \cdot f_3(\phi) \cdot \psi_s \tag{11.5}$$

where ψ_s is a spin factor independent of the spatial coordinates r_1 θ and ϕ. Since the free atom or ion is placed in an environment with O_h symmetry, the wave functions are split into a triply degenerate set, T_{2g} and a doubly degenerate set, E_g.

In a similar manner, we can determine the splitting of various sets of orbitals in environments of other symmetries which we may encounter in complexes such as T_d, D_{4h}, D_{2d} and C_{2v}.

The results, we have obtained so far for single electrons in various types of orbitals, apply also to the behaviour of terms arising from group of electrons. Just as a single d electron in a free atom has a wave function which belongs to a five-fold degenerate set corresponding to the five values which m may take in the $f_3(\phi)$ factor of the wave function, so a D state arising from any group of electrons has a completely analogous five-fold degeneracy because of the five values which the quantum number m may take.

The use of subscripts g and u is governed by the following rules. If the point group of the environment has no centre of symmetry, then no subscripts are used, since they cannot have any meaning when the environment does have a centre of symmetry, the subscripts are determined by the type of orbital. All A.O.'s of which the quantum number l is even (s, d, g . . . .) being centrosymmetric and hence of g character, and all A.O.'s for which l is odd (p, f, h . . . .) being antisymmetric to inversion and thus of u character.

Ligands may be thought of as having one particular orbital directed towards the transition metal. If this orbital is tightly bound weak interaction is to be expected. On the other hand, if it is loosely bound strong interaction would be expected. Since the radial function $f_1(r)$ involves no directional variables, it is invariant to all operations in a point group. The function $f_2(\theta)$ depends only upon the angle θ. Therefore if all the rotations are carried out about the axis from which θ is measured, then $f_2(\theta)$ would also be invariant. Thus by choosing the axis of rotations in this way (or, in other words always quantising the orbitals about the axis of rotation) only the function $f_3(\phi)$ will be altered by rotations. The explicit form of the $f_3(\phi)$ function, aside from a normalising constant is

$$f_3(\phi) = e^{im\phi} \tag{11.6}$$

and the five d orbitals are those in which m takes the values 2, 1, 0, −1, −2.

If we take the function $e^{im\phi}$ and rotate by an angle α the function becomes $e^{im(\phi+\alpha)}$. Thus we can easily see that the set of $f_3(\phi)$ wave functions I, becomes II on rotation by α

$$\underset{\text{I}}{\begin{bmatrix} e^{2i\phi} \\ e^{i\phi} \\ e^{0} = 1 \\ e^{-i\phi} \\ e^{-2i\phi} \end{bmatrix}} \xrightarrow[\text{angle } \alpha]{\text{rotation by}} \underset{\text{II}}{\begin{bmatrix} e^{2i(\phi+\alpha)} \\ e^{i(\phi+\alpha)} \\ e^{\alpha} \\ e^{-i(\phi+\alpha)} \\ e^{-2i(\phi+\alpha)} \end{bmatrix}}$$

The matrix necessary to produce this transformation is

$$\begin{bmatrix} e^{2i\alpha} & 0 & 0 & 0 & 0 \\ 0 & e^{i\alpha} & 0 & 0 & 0 \\ 0 & 0 & e^{0} & 0 & 0 \\ 0 & 0 & 0 & e^{-i\alpha} & 0 \\ 0 & 0 & 0 & 0 & e^{-2i\alpha} \end{bmatrix}$$

For a two-fold rotation, $\alpha = \pi$ and hence, the sum of the diagonal elements is $\frac{\sin 5\pi/2}{\sin \pi/2} = 1$

Similarily for the three-fold and four-fold rotations

$$\chi\,(C_3) = \frac{\sin 5\pi/3}{\sin \pi/3} = -1$$

$$\chi\,(C_4) = \frac{\sin 5\pi/4}{\sin \pi/4} = -1 \tag{11.7}$$

In the present case

$$\chi\,(E) = 5$$

The representation we have derived is reducible to $E + T_2$. In the group O_h we will have, since the d wave functions are inherently g in their inversion property:

In general, the strength of a ligand field increases in the series, halogen (e.g. F) $<$ oxygen ligands (e.g. H_2O) $<$ nitrogen ligands (e.g. NH_3) $<$ carbon ligands (e.g. CN^-).

An increase in formal ionic charge will cause the ligands to be more attracted towards the central atom. Crystal field theory regards the electrostatic attraction between the ionic or highly polar ligand (e.g. Cl^-, H_2O) and the positively charged cation as responsible for the stability of a complex. The forces involved are similar to these which hold an ionic crystal together hence the name of the theory. The essential point made by the theory is the recognition that, although in an isolated cation the degeneracy of all five d orbitals is maintained, in an octahedral crystal field the degeneracy is removed.

It is usual to choose the cartesian axes of an octahedral complex to be the four field axes of the octahedron. It follows that p orbitals are still degenerate in the complex, for all exactly equivalent positions with respect to the ligands. This may not be true

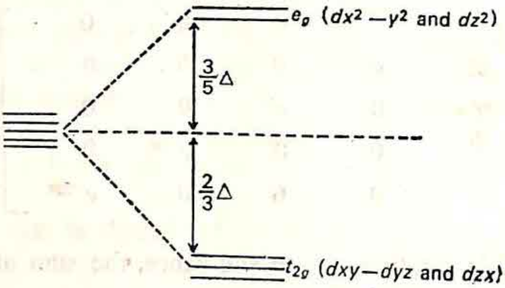


Fig. 11.3. Splitting of *d* orbitals.

for the *d* orbitals. Two, $d_{x^2-y^2}$ and d_{z^2} point along the axes whilest the other three d_{xy}, d_{yz} and d_{zx} are directed between the axes. These sets will have different energy.

The separation between the t_{2g} and e_g orbitals is denoted by Δ or 10 D_q which varies from complex to complex.

There are two limiting cases.

i) Δ may be small (the high spin or 'weak-field' case).

ii) Δ may be large (the 'low-spin' or 'strong-field' case).

In the weak field case, electrons are added successively in *d* orbitals as follows (number of unpaired electrons and spin multiplicity are also given below).

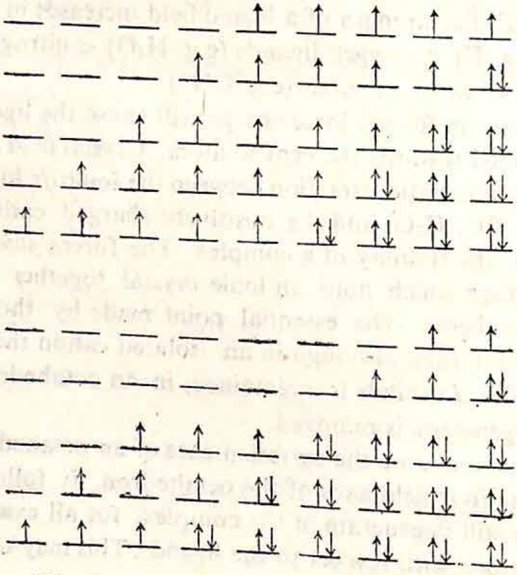


Fig. 11.4. Successive addition of *d* orbitals.

Number of unpaired electron	1	2	3	4	5	4	3	2	1
Spin multiplicity	2	3	4	5	6	5	4	3	2

The electron distribution in strong-field (low-spin) complexes

Number of unpaired electron	1	2	3	2	1	0	1	2	1
Spin multiplicity	2	3	4	3	2	1	2	3	2

'High-spin' and 'low-spin' are phenomenological terms, 'weak field' and 'strong field' describe the magnitude of the crystal field.

11.6.1 SPIN-ORBIT COUPLING

Spin-orbit coupling is invariably weaker than the crystal field interaction in the ions of the first transition series, it frequently has to be taken into account for a detailed understanding of the electronic spectra and magnetic properties of complexes.

11.7 Electronic Spectra of Transition Metal Complexes

The visible and ultraviolet spectra of transition metal complexes show three types of bonds.

a) sharp, weak,
b) broad, weak, and
c) broad, strong.

The first two of these are accounted for by the crystal field theory. For the explanation of the third, ligand-field theory is required. The weak bonds are all associated with forbidden electronic transitions involving the excitation of an electron from one *d* orbital to another. The relative positions of these weak bonds are readily correlated with energy level diagrams based on octahedral crystal field.

The strong broad bonds which generally appear at the short wave-length end of the spectrum are due to transitions of an electron from one of the bonding molecular orbitals (largely located on the ligands) to either on e_g or t_{2g} orbital (largely located on the metal). These transitions are accompanied by a charge migration from the ligand to the metal and are called charge-transfer transitions.

The spectra of weak field complexes are the easiest to interpret quantitatively. For the intermediate case, which occurs frequently in practice, second-order interactions are important and large secular determinants may have to be solved.

CHAPTER 12

Weak Chemical Interaction

12.1 London Interaction

In the previous chapters we have mainly discussed the theory of the covalent bond where the electron delocalisation is responsible for binding energy. However, there are interactions between chemical species which do not involve such electron delocalisation. One of the example of such interaction is the van der Waals interaction which is responsible for holding non-polar molecules together in liquids and solids.

The origin of van der Waals interaction is difficult to conceive. A neutral molecule has a spherically-symmetrical charge distribution and it has no permanent dipole moment. Yet, such molecules have a tendency to aggregate as liquids or solids. The answer is that such a molecule (or atom) could possess an instantaneous dipole moment, the time average of which is zero. This instantaneous dipole introduces a moment in a neighbouring

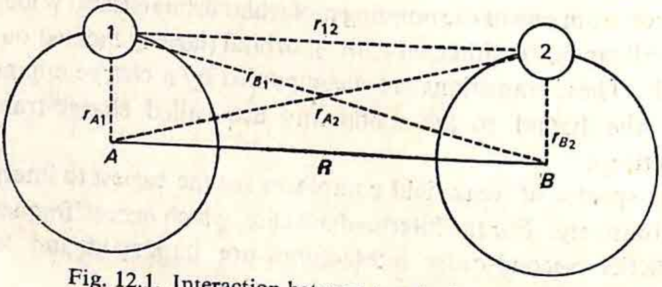


Fig. 12.1. Interaction between two hydrogen atoms.

molecule which causes interaction between the instantaneous dipole and the induced dipole. This is called van der Waals interaction or London interaction.

We shall now try to calculate the interaction energy between two hydrogen atoms *A* and *B* when the internuclear distance *R* is large so that electron clouds do not overlap. The wave-function for the hydrogen atoms *A* and *B* is perturbed on account of the following factors.

i) Interaction due to electron (1) and nucleus *B*.
ii) Interaction due to electron (2) and nucleus *A*.
iii) Interaction between nuclei *A* and *B*.
iv) Electron repulsion between electron (1) and (2).

The present case differs from the case of hydrogen molecule since electron 1 and 2 are not interchangeable. The unperturbed wave function for the system is given by

$$\psi^{\circ} = \psi_A^{(1)} \psi_B^{(2)} \tag{12.1}$$

where ψ_A and ψ_B are 1*s* have functions. The perturbation H' in the Hamiltonian is given by

$$H' = -\frac{e^2}{r_{B1}} - \frac{e^2}{r_{A2}} + \frac{e^2}{R} + \frac{e^2}{r_{12}} \tag{12.2}$$

where r_{B1}, r_{A2}, r_{AB} and r_{12} have the meaning as indicated in the diagram. Let us suppose that the coordinates of the first electron relative to the nucleus are x_1, y_1, z_1, while coordinates of the second electron relative to the nucleus are x_2, y_2 and z_2. Equation (12.2) can be expressed as a Taylor's series in inverse power of *R*, so that we have

$$\begin{aligned} H' = {} & \frac{e^2}{R^3}(x_1 x_2 + y_1 y_2 - 2 z_1 z_2) + \frac{3}{2}\frac{e^2}{R^4}\{(r_1^2 z_2 - r_2^2 z_1) + \\ & (2 x_1 x_2 + 2 y_1 y_2 - 3 z_1 z_2)(z_1 - z_2)\} + \frac{3}{4}\frac{e^2}{R^5}(r_1^2 r_2^2 - \\ & 5 r_2^2 z_1^2 - 5 r_1^2 z_2^2 - 15 z_1^2 z_2^2) + 2 (x_1 x_2 + y_1 y_2 + 4 z_1 z_2)^2 \end{aligned} \tag{12.3}$$

The significance of various terms in equation (12.3) is as follows:

i) The first term represents the interaction between the instantaneous dipoles of the two atoms.

ii) The second term represents the dipole-quadrupole* interaction.

iii) The third term represents the quadrupole-quadrupole interaction and so on.

For simplicity we shall ignore (ii) and (iii) for the time being so that

$$H' = \frac{e^2}{R^3} (x_1 x_2 + y_1 y_2 - 2 z_1 z_2) \tag{12.4}$$

and the interaction energy E'' is given by

$$E'' = \int \psi^{\circ *} (H')^2 \psi^{\circ} d\tau \tag{12.5}$$

which on solving yields,

$$E'' = -\frac{6 e^2 a_0^5}{R^6} \tag{12.6}$$

where a_0 = Bohr's radius. For deriving equation (12.6) an approximate second order perturbation treatment is employed, the details of which are given in the appendix.

When the second and third term in equation (12.3) are also taken into account, the interaction energy is given by

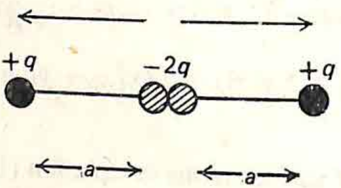
$$E'' \cong -\frac{6 e^2 a_0^5}{R^6} - \frac{135 e^2 a_0^7}{R^8} - \frac{1416 e^2 a_0^9}{R^{10}} \tag{12.7}$$

An approximate method of estimating the van der Waals forces between two atoms or molecules A and B on molecular polarisability has been suggested by London. Accordingly, van der Waals interaction energy may be written as

$$E'' = -\frac{6 n_A n_B e^4 \overline{Z}_A^2 \overline{Z}_B^2}{R^6 (I_A + I_B)} \tag{12.8}$$

---

*Below is an example of a typical electric quadrupole.



It consists of two dipoles whose effects at external points do not cancel. Quadrupole moment of the charge distribution Q is defined by

$$Q = 2 q a^2$$

where n = number of effective electrons.

$\overline{Z}^2$ = average value of z^2 for these electrons.

Z = coordinate of the electron relative to the nucleus in the field direction.

I = energy difference between the normal state and the effective zero-point energy which is approximately equal to the first ionisation energy.

The subscript A and B denote the quantity corresponding to the type of molecules.

Since polarisability α for a particular species is given by

$$\alpha \cong \frac{2n\, e^2\, \overline{Z}^2}{I} \tag{12.9}$$

Equation (12.8) can be written as

$$E'' = -\frac{3}{2}\,\frac{\alpha_A\,\alpha_B}{R^6}\,\frac{I_A\,I_B}{I_A + I_B} \tag{12.10}$$

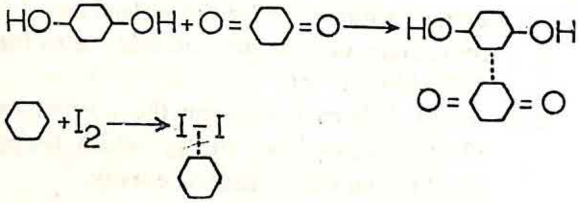
When the molecules are identical i.e. $I_A = I_B = I$ and $\alpha_A = \alpha_B = \alpha$ we have

$$E'' = -\frac{3}{4}\,\frac{\alpha^2\, I}{R^6} \tag{12.11}$$

Thus, quantum mechanics tells us that attraction energy between non-polar molecules varies inversely as the sixth power of inter-nuclear distance.

12.2 Donor Acceptor Interaction

An electron donor molecule has weakly bound electrons and a corresponding low ionisation potential. The electron acceptor has a low lying vacant orbital having high electron affinities. The two types of molecules can interact to form a donor-acceptor complex with a much lower binding energy as compared to covalent molecules. A typical example is the formation of green quinhydrone from colourless hydroquinone (donor) and yellow quinone (acceptor). Iodine forms such a complex in benzene with an absorption band at 3000 Å which does not occur in the spectra of either iodine or benzene. The stability and the characteristic electronic absorption bands can be easily explained on the basis of quantum mechanical treatment given by Mülliken. Typical examples of formation of charge-transfer complexes are as follows.



(i)

(ii)

Let the wave function of separate donor and acceptor molecules be ψ (D) and ψ (A) respectively. When they are separated, the wave function of the pair can be written as

$$\psi_{(D,\,A)} = \psi_{(D)}\,\psi_{(A)} \tag{12.12}$$

However if we consider a pair of ions D^+ and A^- separated by a large distance, the wave function for such a system would be given by

$$\psi_{(D^+,\,A^-)} = \psi_{(D^+)}\,\psi_{(A^-)} \tag{12.13}$$

Equations (12.12) or (12.13) would not be the true representation of the situation when the donor and acceptor molecules are brought together in order to overlap the electron clouds. Since, there would be a possibility of electron-exchange, the total wave function for the complex may be written as,

$$\psi = a\cdot\psi_{(D,\,A)} + b\cdot\psi_{(D^+,\,A^-)} \tag{12.14}$$

in order to account the two possibilities postulated by equations (12.12) and (12.13). a and b are constants. The coefficients can be solved by solving relevant secular equations. Two solutions are obtained and the wave functions can be written as

$$\psi_1 = a_1\,\psi_{(D,\,A)} + b_1\,\psi_{(D^+,\,A^-)} \tag{12.15}$$

$$\psi_0 = a_0\,\psi_{(D,\,A)} + b_0\,\psi_{(D^+,\,A^-)} \tag{12.16}$$

where a_1, b_1, a_0 and b_0 are constants. The stability of the complex can be explained as follows. The energy of the wave function ψ_0 is less than the energy of either $\psi_{(D,\,A)}$ or $\psi_{(D^+,\,A^-)}$. The energy level diagram is given in Fig. 12.2.

The characteristic absorption band of the complex occurs due to electronic transition $\psi_0 \rightarrow \psi_1$. It should be noted that $\psi_{(D,\,A)}$ is called the no-bond state and $\psi_{(D^+,\,A^-)}$, the ionic or charge transfer state. In the case of weak charge-transfer complexes, the

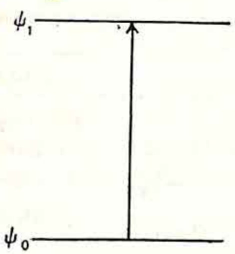


Fig. 12.2. Energy levels of charge-transfer complexes.

energy of the transition $\psi_0 \rightarrow \psi_1$, equals the energy of transition $\psi_{(D,\,A)} \rightarrow \psi_{(D^+,\,A^-)}$ so that it can be shown that

$$h\,\nu_{CT} = E\,(D^+, A^-) - E\,(D, A) = I\,(D) - A\,(A) + Q \quad (12.17)$$

In equation (12.17) Q is the coulomb energy between D^+ and A^- and ν_{CT} is the frequency of charge-transfer bond. The energy is calculated with the help of second-order perturbation theory. Equation (12.7) is found to be valid in a number of cases. However this is applicable only to interactions which are sufficiently weak.

Alternative theories* of charge-transfer complexes are based on simple molecular orbital treatment and free electron model.

12.3 Hydrogen Bonding

The hydrogen bond *A-H*, . . . , *B* is a specific molecular interaction, where *B* represents the elements of the second row of the periodic table e.g. *B*, *C*, *N*, *O* and *F*. Weaker hydrogen bond interaction occurs with sulphur and halogens. In hydrogen bond interaction, the proton must be situated far out of the electron cloud of the donor atom *A* and must penetrate the electron cloud of the acceptor atom *B* deep enough. Some of the functional groups acting most frequently as proton donors and acceptors are summarised in the Table 12.1.

Following theories have been advanced to explain hydrogen bonding.

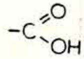
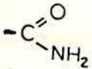
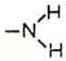
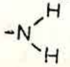
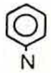
1) THE ELECTROSTATIC THEORY

Since the proton is hydrogen nuclei, its electrostatic field would

---

*Dewar, M.J.S. and Leplay, A.R. I. *Amer. Chem. Soc. 83*, 4560 (1961).

Table 12.1. Functional groups acting as proton donors and acceptors

Proton donors		Proton acceptors	
		(a) Oxygen in	
Carboxylic acids		Carbonyl group	>C=O
		ethers	>O
Alcohols	O–H	alcohols	O–H
Amides		(b) Nitrogen in amines	>N: >N–H 
Amines			
		(c) *N*-heterocyclic Compounds	

be intense so that its attraction for the non-bonded electrons on the other atom can be so strong as to lead to bonding. However, all the properties of hydrogen bonds cannot be explained by this model.

2) THE VALENCE-BOND THEORY

In 1953, Coulson developed valence-bond theory of the hydrogen bond. Four electrons involved in *A-H-B* are considered. The ground state for the hydrogen-bonded system is written as

$$\phi = C_1 \phi_1 + C_2 \phi_2 + C_3 \phi_3 \tag{12.18}$$

where C_1, C_2 and C_3 are constants. ϕ_1 corresponds to structure based on dispersion forces, ϕ_2 correponds to the electrostatic structure and ϕ_3 describes the charge-transfer structure. The contributions to total energy due to various structures can be calculated using variation method. The total energy for ice is found to be −8.6 kcal/mole which agrees favourably with the experimental value of −6.1 kcal/mole. The break-up of the energy contribution due to various forces is as follows:

Force	Contribution to total energy
Electrostatic force	−6 kcal/mole
Short range repulsion force	+8.4 ,,
Charge-transfer force	−8.0 ,,
Dispersion forces	−3.0 ,,
	Total energy = 8.6 kcal/mole

3) MOLECULAR ORBITAL THEORY

In the system A-H, . . . , B, we may consider A-H and B separately from the viewpoint of M.O. theory. The molecular orbital ψ_{AH} for A-H can be written as a linear combination of the p-orbital of A and $1s$ orbital of hydrogen atom H, and the orbital for the lone pair of electrons in the atom B may be represented by ψ_B. On solving we get

$$\psi\,(\sigma) = a\,\psi_{AH} + b\,\psi_B$$

and

$$\psi\,(\sigma^*) = a\,\psi_{AH} - b\,\psi_B$$

where $\psi\,(\sigma^*)$ is the anti-bonding orbital and $\psi\,(\sigma)$ denotes the bonding orbital while a and b are constants. The influence of H-bonding on properties of solutions and compounds are given in Table 12.2.

Table 12.2. Hydrogen bonding and the properties of the molecules

Property	Behaviour of H-bonded compounds relative to a non-H-bonded one
Molar volume	Lower
Density	Higher
A-H, . . . , B bond length	Shorter
Viscosity	Higher
Surface tension	Higher
Vapour pressure	Lower
Melting point	Higher
I.R. spectra	Shifted
NMR (Chemical shift)	Shifted
Boiling point	Higher

Thus we note that the origin of weak interactions can be understood on the basis of quantum mechanics. It provided a powerful tool for theoretical derivation of intermolecular potential energy as a function of distance.

APPENDIX: PERTURBATION THEORY OF VAN DER WAALS FORCES FOR HYDROGEN ATOM

The Hamiltonian for two hydrogen atoms separated by a distance such that overlap of orbitals does not take place can be expressed as

$$H = H^\circ + H' + H'' + \ldots$$

where H° is the unperturbed Hamiltonian and H', H'', . . . , are the perturbations of different orders. The corresponding energy eigenvalues are given by

$$H = E^\circ + E' + E'' + \ldots$$

where E° is the unperturbed energy and E', E'' are the perturbation energies of different orders. The first order perturbation energy of a non-degenerate system would be given by

$$E' = \frac{\int \psi^{\overset{*}{\circ}}\, H'\, \psi^\circ\, d\tau}{\int \psi^{\overset{*}{\circ}}\, \psi^\circ\, d\tau}$$

In order to evaluate second-order perturbation energy we need first order perturbed wave-function ψ'.

The second order perturbation energy E'' using first order perturbed wave-function would be given by

$$E'' = \frac{\int \psi^{\overset{*}{\prime}}\, H'\, \psi'\, d\tau}{\int \psi^{\overset{*}{\prime}}\, \psi'\, d\tau}$$

It has been pointed out by Lennard-Jones that the first order perturbed wave-function can be approximately written as:

$$\psi' = \psi^\circ (1 + AH')$$

where $A = \frac{1}{E^\circ}$ and $E^\circ = -e^2/a_0$. Hence, we can write

$$E'' = \int \psi^{\overset{*}{\circ}} (1 + AH')\, H'\, \psi^\circ (1 + AH')\, d\tau$$

$$= \int \psi^{\overset{*}{\circ}}\, H'\, \psi^\circ\, d\tau + A \int \psi^{\overset{*}{\circ}}\, (H')^2\, \psi^\circ\, d\tau$$

to a first approximation.

It can be proved that

$$\int \psi^{\circ *} H' \psi^{\circ} \, d\tau = 0$$

Hence, the first order perturbation energy is zero. The second order perturbation energy would be given by

$$E'' = A \int \psi^{\circ *} H'^{2} \psi^{\circ} \, d\tau$$

$$= -\frac{a_0}{e^2} \int \psi^{\circ *} (H')^2 \psi^{\circ} \, d\tau$$

Substituting the value of H' from equation (12.4) and evaluating the integral, we get

$$E'' = -\frac{a_0}{e^2} \frac{2\, e^4}{3\, R^6}, \; \overline{r_1^2} \; \overline{r_2^2}$$

where $\overline{r_1^2}$ and $\overline{r_2^2}$ are the mean square of the electron-nucleus distance for a Bohr orbit. The values of $\overline{r_1^2}$ and $\overline{r_2^2}$ can be calculated by using the equation

$$\overline{r^2} = \int \psi^{\circ *} r^2 \psi \, d\tau$$

Using hydrogen wave functions, we get

$$\overline{r^2} = 3a_0^2$$

Therefore,

$$E'' = -\frac{a_0}{e^2} \cdot \frac{2\, e^4}{3\, R^6} \cdot 9\, a_0^4 = -\frac{6\, e^2\, a_0^5}{R^6}$$

CHAPTER 13

Elements of Quantum Statistics

In Chapters 3 to 11, Quantum mechanics of simple chemical systems such as atoms and molecules have been discussed. Chemical bonding in molecules has been interpreted in terms of quantum mechanics. Non-chemical interaction between molecules has been discussed in Chapter 12. In this chapter we are concerned with the statistical behaviour of group of molecules or atoms. The logical theoretical tools for the study of such behaviour are kinetic theory and statistical mechanics. We shall not develop Quantum statistics in the chapter as it is understood formally by physicists. The main emphasis here would be on the relation between kinetic theory, statistical mechanics and Quantum mechanics. Attention would be drawn to modifications needed for defining probability density for quantum systems.

13.1 Quantum Effects in Kinetic Theory

In kinetic theory, molecules are treated like rigid spheres and it is assumed that these obey Newtonian mechanics. All the properties of gases are satisfactorily predicted on the basis of such a picture. On the other hand, it becomes necessary to assign wave properties to electrons for which Newtonian laws of motion are completely inadequate to describe their motion. Both molecules and electrons are small particles. The question is, where is the dividing line so far as the application of quantum mechanics and kinetic theory is concerned. According to uncertainty principle;

$$\Delta v, \Delta x \sim a\, h/m$$

where Δv and Δx represent the uncertainty in velocity and position respectively and h is Planck's constant. a is numerical factor, a knowledge of the exact magnitude of which is not significant. Thus, the product $\Delta v . \Delta x$ is greater when m is small. Electrons are much lighter than molecules. Hence, in case of electrons, the position and velocity of electrons cannot be precisely assigned simultaneously. This is not so in case of molecules.

However, when molecules come close to each other quantal effects may become significant. Intuitively, this would depend on the ratio r of de Broglie wave length and the collision diameter σ

$$\text{i.e., } r = \frac{h}{\sqrt{2}\, \pi\sigma\, (m\, kT)^{1/2}}$$

where

m = mass of the molecule
k = Boltzmann constant
T = temperature in °K

Each molecule may be supposed to be surrounded by a wave field so that the effective diameter of molecules would be larger than that predicted by the classical theory. The value of r is less than 1 for helium while for hydrogen it is somewhat larger than that for helium. In fact, serious discrepancies have been observed when viscosity of helium calculated on the basis of kinetic theory (rigid spheres) is compared with the experimental values.

The unusual phase diagram of helium, abnormal properties of helium at low temperature including the deviation from the principle of corresponding state for noble gases are all due to quantum effects. According to the quantum mechanical theorem of corresponding state, the reduced pressure p^* is a function of reduced temperature T^*, reduced volume V^* and λ^* defined by

$$\lambda^* = \frac{h}{\sigma \sqrt{m\, \epsilon^*}} \tag{13.1}$$

where ϵ^* is the force constant in the intermolecular potential $\epsilon\,(r)$ represented by

$$\epsilon\,(r) = \dot{\epsilon}\, f\left(\frac{r}{\sigma}\right) \tag{13.2}$$

Here ϵ is the potential energy and r denotes the intermolecular separation, is equivalent to collision diameter. λ^* takes into account the quantum effects and is related to de Broglie wave length. It is obvious that larger would be λ^*, smaller the value of m and ϵ^*. Although, hydrogen is the lightest molecule, ϵ^* for hydrogen is greater than that for helium. Hence, helium displays much more pronounced quantum effects.

Quantum mechanical theorem of corresponding states was deduced by Byk and de Boer. A brief outline of the deduction is given below. The translational energy level of the system can be obtained by the following Schrödinger equation,

$$\left[-\frac{h^2}{8\pi^2 m}\sum_i \nabla_i^2 + \sum_{i<j}\epsilon^*\varphi\left(\frac{r_{ij}}{\sigma}\right) - E_r\right]\psi_r\,(r_1\, r_2, \ldots, r_N) = 0 \tag{13.3}$$

where ψ_r is the wave function corresponding to the energy level, E_r. ∇_i^2 is the Laplacian operator. $r_1, \ldots, r_N$ denote the positional coordinates of the molecules. If we introduce the reduced variables, then $\tilde{\nabla}_i^2$, the reduced Laplacian is given by;

$$\tilde{\nabla}_i^2 = \frac{\partial^2}{\partial\,(x_{i/\sigma})^2} + \frac{\partial^2}{\partial\,(y_{i/\sigma})^2} + \frac{\partial^2}{\partial\,(z_{i/\sigma})^2}$$

equation (13.3) would be transformed as follows:

$$\left[-\frac{h^2}{8\pi^2 m}\sum \tilde{\nabla}_i^2 + \sum_{i<j}\epsilon^*\varphi\left(\frac{r_{ij}}{\sigma}\right) - \frac{E_r}{\epsilon^*}\right]\psi_r\,(r_1, \ldots, r_N) = 0$$

The reduced energy levels would depend on N, the number of molecules, $\frac{V}{\sigma}$ and $\frac{h}{\sigma\sqrt{m\,\epsilon^*}}$ and hence it can be shown that

$$p^* = f\left(T^*, V^*, \frac{h}{\sigma\sqrt{m\,\epsilon^*}}\right) \tag{13.3}$$

It should be noted that $\lambda^* \to 0$ for heavy molecules and classical approximation is valid. Values of λ^* for a few gases are recorded in Table 13.1.

Table 13.1. λ^* **for gases**

Gases	λ^*
H_2	1.729
HD	1.412
He	3.000
He^3	2.67
Ne	0.593
A	0.186
Kr	0.102
Xe	0.064
CH_4	0.239
N_2	0.226
CO	0.220

13.2 Relationship of Quantum Mechanics and Statistical Mechanics

Statistical mechanics and quantum mechanics are interrelated in many ways. In one of the methods of the derivation of Maxwell-Boltzman distribution law, it is assumed that the allowed energy levels for the particles (atoms, molecules, etc.) are known from quantum mechanics.

For evaluation of partition function in statistical mechanics, allowed values of rotational energy E_r, translational energy E_t and vibrational energy E_{vib} are needed. These are given in Table 13.2. E_r and E_{vib} are evaluated as follows.

13.2.1. a) RIGID DIATOMIC ROTOR

The motion of two particles of m_1 and m_2 which are joined by a rigid connection of length R so that their centre of mass always remains at rest, is equivalent to the motion of a single particle of reduced mass μ at a distance R from origin of coordinates. For such a purely rotational motion $V = 0$, so that the Schrödinger equation for the system would be given by:

$$-\frac{h^2}{8\pi^2\mu}\nabla^2\psi = E\psi \qquad (13.4)$$

In terms of polar coordinates this would be written as

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\psi}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\theta^2}+\frac{8\pi^2 I}{h^2}E\psi = 0 \quad (13.5)$$

On solution, the rotational energy levels E^j_{rot} are given by

$$E^j_{\text{rot}} = J(J+1)\frac{h^2}{8\pi^2 I} \tag{13.6}$$

where $J = 0, 1, 2, \ldots,$ and is called rotational quantum number

b) HARMONIC OSCILLATOR

The Schrödinger equation for harmonic oscillator is written as:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}[E - V(x)] = 0 \tag{13.7}$$

where the potential energy $V(x)$ for harmonic oscillator is given by

$$V(x) = \tfrac{1}{2}Kx^2 \tag{13.8}$$

K is called the force constant and is related to the frequency ν by the relation $K = 4\pi^2\nu^2\mu$. Thus, the wave equation for harmonic escillator becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}[E - 2\pi^2\nu^2\mu\cdot x^2]\psi = 0 \tag{13.9}$$

It can be solved by rewriting it as:

$$\frac{d^2\psi}{dx^2} + [\epsilon - \alpha^2 x^2]\psi = 0 \tag{13.10}$$

where

$$\epsilon = \frac{8\pi^2\mu E}{h^2} \text{ and } \alpha^2 = \frac{16\pi^4\mu^2\nu^2}{h^2} \tag{13.11}$$

On solution, the above equation yields the energy values

$$E_\nu = (v + \tfrac{1}{2})h\nu \tag{13.12}$$

where v is called the vibrational quantum number which can have the values 0, 1, 2, 3, . . .

13.2.2 MAXWELL-BOLTZMANN STATISTICS

Following assumptions are made in the derivation of Maxwell-Boltzmann statistics:

1) Individual particles are supposed to be indistinguishable.
2) Any number of parcticles can be assigned to any level.

In case of elementary particles or a system of species containing number of particles, restrictions are imposed due to Pauli Exclusion Principle according to which no more than one particle can go into each energy level. Thus, in case of electrons, one electron will occupy one specific energy level. Further, if the particles considered are composed of an even number of elementary particles, any number can be accommodated in a single energy level. These two situations give rise to Fermic-Dirac and Bose-Einstein statistics as described in Table 13.3.

Table 13.2. Allowed values of energies needed for computation of partition function

Type of energy	Allowed values of energy	Obtained by the solution of the appropriate Schrödinger equation for
Translational energy	$E_t = \frac{n^2 h^2}{8ma^2}$	a free particle in one dimension along the length a
Rotational energy	$E_r = \frac{J(J+1) h^2}{8 \pi^2 I}$	a rigid-rotor model for a diatomic molecule.
Vibrational energy	$E_{vib} = (v + \frac{1}{2}) h$	a harmonic oscillator

Table 13.3. Fermi-Dirac and Bose-Einstein statistics

Fermi-Dirac statistics $N_j = \frac{g_i}{\exp(\alpha+\beta \epsilon_j)+1}$ N_j = number of particle in the jth level g_i = degeneracy factor	Applied to odd number of elementary particles (e.g., electrons, protons) α and β are constants	With the restriction that there is only one particle per state
Bose-Einstein statistics $N_j = \frac{g_i}{\exp(\alpha+\beta \epsilon_i)-1}$	Applied to even number of elementary particles (e.g., deuterons, photons)	The particles are distinguishable but there could be any number of particle per state

13.3 Quantum Statistics

In classical mechanics, the state of a system is described by its position and momentum coordinates in space. In quantum mechanics such a precise specification of state is not possible on account of Heisenberg's Uncertainty Principle. Thus, in quantum mechanics, the state of a system is described by a wave function ψ. For a single particle, ψ, is a function of coordinates x, y, z and t, i.e., $\psi\ (x, y, z, t)$ or (q, t).

(q, t) can be expanded in terms of a complete set of normalised orthonormal basis functions as follows:

$$\psi\ (q, t) = \sum_k a\ (k, t)\ u\ (u, q) \tag{13.13}$$

where $u(k, q)$ denotes the set of normalised orthonormal basis function having a probability amplitude as $a(k, t)$.

The probability density $W\ (q, t)$ would be given as

$$W\ (q, t) = \psi^* \psi = a^*\ (k, t)\ a\ (k, t) \tag{13.14}$$

where * represents the complex conjugate. Here $W(q, t)$ is the probability of finding a system in the state characterised by value k. It follows that

$$\sum W\ (q, t) = \sum_k a^*\ (k, t)\ a\ (k, t) = 1 \tag{13.15}$$

The probability amplitude $a\,(k, t)$ is related to density matrix ρ_{mn} as follows

$$\rho_{mn} = \frac{1}{n} \cdot \sum_{d=1} a^*\ (m, t)\ A\ (n, t) = a^*_m\ a_n \tag{13.16}$$

The mean probability density W_n can be written as

$$\overline{W}_n = P_{nn} = \overline{a^*_n\ a_n} \tag{13.17}$$

ρ_{nn} are the diagonal elements of the density matrix. It is obvious that

$$\sum P_{nn} = \sum W_n = \sum_n a^*_n\ a_n \tag{13.18}$$

In equation (13.18) $\sum\limits_n \rho_{nn} =$ sum of the diagonal elements of the density matrix. This sum is called the trace of a matrix. Hence,

$$\sum_n \rho_{nn} = \sum_n \overline{a^*_n\ a_n} = \text{Trace}\ \rho = 1. \tag{13.19}$$

The implications of equation (13.16), (13.17) and (13.18) are as follows:

a) The density matrix is Hermitian and can be finite or infinite.

b) Equation (13.17) gives the probability that a system chosen at random from the ensemble is found in a state characterised by the value n_c.

c) The diagonal elements of a density matrix are always positive and their sum necessarily equals one.

d) All the systems of the ensemble are found in the same quantum mechanical state defined by non-vanishing eigen values of the density matrix. In terms of density matrix entropy would be given by

$$S = k \text{ trace } \rho\, l_n\, \rho \tag{13.20}$$

It should be noted that the classical operation of integrating the density ρ over the whole space is replaced in quantum mechanics by the process of taking the sum over all diagonal elements of the density matrix or the trace of the matrix.

The above equation can be written in alternative way in the following form:

$$S = -\frac{k}{2} \ln (\text{trace } \rho^2) \tag{13.21}$$

CHAPTER 14

Mathematical Techniques

14.1 Determinant

Consider the simultaneous equations in variables x_1 and x_2

$$a_{11}\,x_1 + a_{12}\,x_2 = h_1 \tag{14.1}$$

$$a_{21}\,x_1 + a_{22}\,x_2 = h_2 \tag{14.2}$$

where a_{ij} and h_i $(i, j = 1, 2)$ are constants

On solving, we have

$$x_1 = (h_1\,a_{22} - h_2\,a_{12})/(a_{11}\,a_{22} - a_{12}\,a_{21}) \tag{14.3}$$

$$x_2 = (h_2\,a_{11} - h_1\,a_{21})/(a_{11}\,a_{22} - a_{12}\,a_{21}) \tag{14.4}$$

The expressions in the numerator and denominator of both solutions arise from the familiar procedure of cross-multiplication to bring about elemination, for example

$$\begin{tikzcd} a_{11} \arrow[dr] & a_{12} \arrow[dl] \\ a_{21} & a_{22} \end{tikzcd}$$

yielding $a_{11}\,a_{22} - a_{12}\,a_{21}$

which we can represent as $\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}\,a_{22} - a_{12}\,a_{21}$

Using equations (14.3) and (14.4) we can solve the following equation

$$4x + 5y = 7$$

$$3x - 10y = 19$$

yielding $x = 3$, and $y = 1$

Let us consider the determinants

$$\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} \text{ or } \begin{vmatrix} a_2 & b_2 \\ a_1 & b_1 \end{vmatrix}$$

$$= a_1\, b_2 - a_2\, b_1 \quad \text{or} \quad a_2\, b_1 - a_1\, b_2$$

The products $a_1\, b_2$, $a_2\, b_1$ are called the elements of the determinant; $a_1\, b_1\, a_2$, b_2 are the constituents of the determinant. When only two elements are involved, the determinant is said to be of second-order.

14.1.1 Expansion of a Determinant

Let us consider the determinant

$$\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} = 0$$

which can be expanded as follows

$$a_1 \begin{vmatrix} b_2 & c_2 \\ b_3 & c_3 \end{vmatrix} b_1 \begin{vmatrix} c_2 & a_2 \\ c_3 & a_3 \end{vmatrix} + c_1 \begin{vmatrix} a_2 & b_2 \\ a_3 & b_3 \end{vmatrix} = 0$$

Thus the determinant is expanded by reducing the determinant to lower order.

14.1.2 Fundamental Properties of a Determinant

The properties of a determinant are listed below:

1) The value of a determinant is not altered by changing the columns into rows or the rows into columns. For example

$$\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} = \begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix}$$

2) The sign, not the numerical value of a determinant is altered by interchanging any two rows, or any two columns. Thus

$$\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} = - \begin{vmatrix} b_1 & a_1 \\ b_2 & a_2 \end{vmatrix}$$

3) If two rows or two columns of a determinant are identical,

the determinant is equal to zero. Thus,

$$\begin{vmatrix} a_1 & a_1 & c_1 \\ a_2 & a_2 & c_2 \\ a_3 & a_3 & c_3 \end{vmatrix} = 0$$

4) When the constituents of two rows or two columns differ by a constant factor, the determinant is equal to zero. Thus,

$$\begin{vmatrix} 4 & 1 & 5 \\ 8 & 2 & 6 \\ 12 & 3 & 7 \end{vmatrix} = 4 \begin{vmatrix} 1 & 1 & 5 \\ 2 & 2 & 6 \\ 3 & 3 & 7 \end{vmatrix} = 4 \times 0 = 0$$

5) If a determinant has a row or column of cyphers it is equal to zero. Thus,

$$\begin{vmatrix} 0 & b_1 & c_1 \\ 0 & b_2 & c_2 \\ 0 & b_3 & c_3 \end{vmatrix} = 0$$

6) Multiplication by a factor is done as follows:

$$m \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} = \begin{vmatrix} ma_1 & b_1 & c_1 \\ ms_2 & b_2 & c_2 \\ ma_3 & b_3 & c_3 \end{vmatrix}$$

7) One row or column of any determinant can be reduced to unity. For example

$$\begin{vmatrix} 3 & 4 & 6 \\ 2 & 8 & 8 \\ 6 & 7 & 9 \end{vmatrix} = 12 \begin{vmatrix} 1 & 1 & 1 \\ 1 & 3 & 2 \\ 8 & 7 & 6 \end{vmatrix}$$

8) If each constituent of a row or column can be expressed as the sum or difference of two or more terms, the determinant can be expressed as the sum or difference of two other determinants. Thus,

$$\begin{vmatrix} a_1 \pm p & b_1 & c_1 \\ a_2 \pm q & b_2 & c_2 \\ a_3 \pm r & b_3 & c_3 \end{vmatrix} = \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} \pm \begin{vmatrix} p & b_1 & c_1 \\ q & b_2 & c_2 \\ r & b_3 & c_3 \end{vmatrix}$$

14.2 Matrices

Let us consider the following set of equations

$$a_{11}\,x_1 + a_{12}\,x_2 + \ldots + a_{1n}\,x_n = y_1$$

$$a_{21}\,x_1 + a_{22}\,x_2 + \ldots + a_{2n}\,x_n = y_2$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$a_{m1}\,x_1 + a_{m2}\,x_2 + \ldots + a_{mn}\,x_n = y_m$$

We can arrange the above in an abbreviated way by writing

$$\begin{bmatrix} a_{11} & a_{12} \ldots a_{1n} \\ a_{21} & a_{22} \ldots a_{2n} \\ \text{—} & \text{—} \ldots \text{—} \\ \text{—} & \text{—} \ldots \text{—} \\ a_{m1} & a_{m2} \ldots a_{mn} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \text{—} \\ \text{—} \\ x_m \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \\ \text{—} \\ \text{—} \\ y_m \end{bmatrix}$$

The first set of detached coefficients a_{ij} set out in m rows and n columns is called a matrix of order m by n or $m \times n$. The numbers a_{ij} are called elements of the matrix, a_{ij} being the element of i^{th} row and j^{th} column. The matrix as a whole is denoted by $[A]$ or by $[a_{ij}]$.

The algebra of matrices has a very close resemblance to the algebra of ordinary numbers. There are rules by which matrices A and B can be added, subtracted, multiplied and divided. These are,

i) Addition of matrices

$$A + B = [a_{ij}] \neq [b_{ij}] = [a_{ij} + b_{ij}]$$

To add together two matrices A and B of the same order $m \times n$, we add their corresponding elements and take the sums as the corresponding elements of the sum matrix which is denoted by $A + B$.

ii) Scalar multiplication

To multiply a matrix A by a scalar number λ, we multiply all elemets a_{ij} by λ

iii) Matrix multiplication

$$BA = C$$

where B is of order $m \times n$
A is of order $n \times p$
C is of order $m \times p$

The multiplication is possible only if the number of columns in B is the same as the number of rows in A.

We discuss below three types of Matrices viz., Unit Matrix, Scalar Matrix, Diagonal Matrix. Consider the following set of equations.

$$y_1 = x_1$$

$$y_2 = \ldots x_2$$

$$y_3 = \ldots\ldots x_3$$

The matrix is

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \text{ is called unit matrix}$$

It is denoted by I such that

$$a_{ii} = 1$$

$$a_{ij} = 0$$

$$i \neq j$$

14.2.1 SCALAR MATRIX

λI is a scalar matrix defined by

$$\lambda I = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{bmatrix}$$

In symbols

$$\lambda A = \lambda IA = A\lambda I = \lambda\ \lambda.$$

Diagonal matrix-A square matrix with its non-diagonal elements zero is called a diagonal, or quasi-scalar matrix. It is thus defined by $a_{ij} = 0,\ i \neq j$. Thus, following would be examples of diagonal matrix.

$$\begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} \text{ or } \begin{bmatrix} a_{11} & 0 & 0 & 0 \\ 0 & a_{22} & 0 & 0 \\ 0 & 0 & a_{33} & 0 \\ 0 & 0 & 0 & a_{44} \end{bmatrix}$$

The matrices, under suitable restrictions upon their orders, obey the following laws,

$$A + B = B + A, \quad A + (B + C) = (A + B) + C$$

$$A\,(B+C) = AB + AC, \; (B + C)\,A = BA + CA$$

which are the ordinary laws of elementary algebra, except for the omission of the commutative law of multiplication.

14.2.2. TRANSPOSITION

From matrix A we may construct a new matrix the rows of which are the columns of A, and consequently the columns of which are the rows of A.

The resulting matrix is called the transpose of A and is denoted by A'. The operation is called transposition. This has no analogue in ordinary algebra. Symbolically, the operation is represented as

$$A' = [a_{ij}]' = [a_{ij}]$$

For example, if

$$A = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \end{bmatrix}$$

then

$$A' = \begin{bmatrix} a_1 & a_2 \\ b_1 & b_2 \\ c_1 & c_2 \end{bmatrix}$$

A symmetric matrix is one which is unaltered by transposition, so that $A' = A$. It follows that such a matrix must be square and symmetrical about its principal diagonal so that $a_{ji} = a_{ij}$.

If $A' = A$, and $a_{ji} = -a_{ij}$, the matrix A is called skew symmetric or antisymmetric.

For example,

$$A = \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix} \text{ is symmetric}$$

$$A = \begin{vmatrix} o & a & b \\ -a & o & c \\ -b & -c & o \end{vmatrix} \text{ is skew symmetric}$$

14.2.3. COMPLEX CONJUGATE OF A MATRIX

If the element of A are complex number a_{ij}, we denote their complex conjugate by $\bar{a}_{ij}$. The matrix $[\bar{a}_{ij}]$ is denoted by $\bar{A}$ and is called the complex conjugate of A.

If $\bar{A}' = A$ the matrix A is square and is unchanged by the operations of transposition and taking complex conjugates. Such a matrix is called Hermitian. However, if $\bar{A}' = -A$, the matrix A, which is square is called skew Hermitian or anti-Hermitian.

14.3 Operator

An operator is a symbol for mathematical procedure that changes one function into another. For example the symbol $\surd$ represents the operation of taking a square root. A list of some typical operators along with the result of their operation on the function which is called operand is given in Table 14.1. These operations can be written in the form of the following equation,

Table 14.1 Some typical operators

Operation	Operator	Result of operation on Y
1. Multiplication by the constant c	$c.$	$c.\,y$
2. Taking the square	$(\quad)^2$	Y^2
3. Differentiation with respect to x	$\frac{d}{dx}$	$\frac{dy}{dx}$
4. Integration with respect to x	$\int (\quad)\,dx$	$\int y\,dx$
5. Addition of x	$x +$	$x+y$

$$(\text{operator}) \times (\text{function}) = (\text{new function})$$

In the Schrödinger equation

$$H\psi = E\psi$$

$$H = \left(V - \frac{h^2}{8\pi^2 m} \nabla^2 \right) \text{ is an operator}$$

If a body is rotated by 180° about the z axis, the x, y and z axes themselves being fixed in space, then $f(x, y, z)$ will be changed into a new function $f'(x\ y\ z)$. This is an operation in the sense described above.

This operation is denoted by the symmetry operation. Another symmetry operator is σ_{xy} which represents the reflection of a body in the $x-y$ plane.

Operators which involve differentiation are called differential operators. Such as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

If a function f and an operator α are related as follows:

$$\alpha f = af$$

where a is a number. Then f is said to be an eigenfunction of the operator α and a is said to be its eigenvalue. Thus in the equation

$$H\psi = E\psi$$

ψ is the eigenfunction and E is the eigenvalue. Similarly since

$$\frac{d}{dx}(e^{2x}) = 2\, e^{2x}$$

e^{2x} is an eigenfunction and 2 is the eigenvalue.

14.3.1. ALGEBRA OF OPERATORS

If α, β and γ represent three different operations, then the expression

$$\alpha\, \beta\gamma\; f(x)$$

means that we first operate on $f(x)$ with γ and then operate on the resultant with β and finally operate on the resultant of the last process with α. The order of application of the operators is always from right to left as they are written.

If the result of the two operations is the same irrespective of the order of operation, the two operators are said to commute, so that

$$\alpha\, \beta\, f = \beta\, \alpha\, f$$

New operators can be formed by adding and subtracting operators. Thus if α and β are operators, we have

$$\alpha f + \beta f = (\alpha + \beta) f$$

$$\alpha f - \beta f = (a - \beta) f$$

$(\alpha + \beta)$ and $(\alpha - \beta)$ are the new operators.

14.4 Functions

If we plot a certain quantity depending on x against x and if we get a well-defined curve, we call this quantity as a function of x and denote it by $f(x)$. If $f(x) = \cos x$ and $f(x) = x^2$, we will get the curves as shown in Fig. 14.1. There is no break in the curve in either case, hence $f(x)$ is continuous for the two cases.

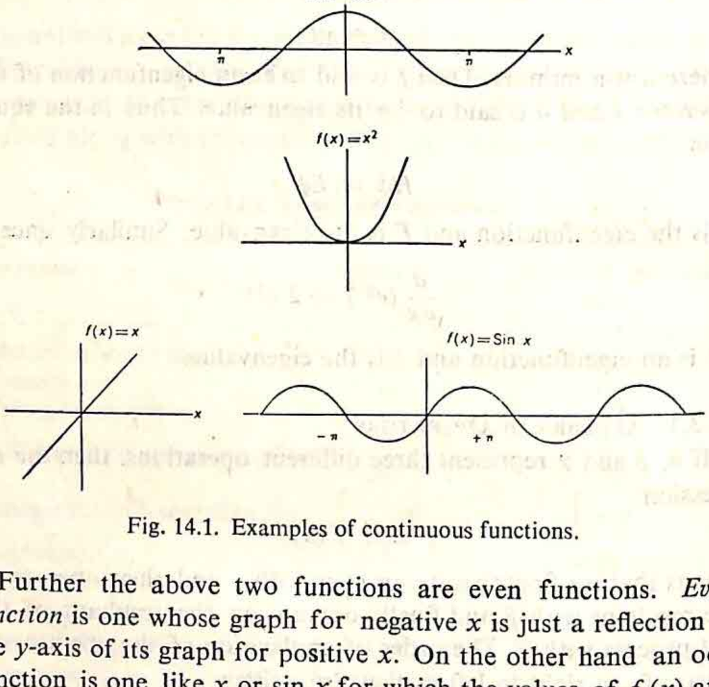


Fig. 14.1. Examples of continuous functions.

Further the above two functions are even functions. *Even function* is one whose graph for negative x is just a reflection in the y-axis of its graph for positive x. On the other hand an odd function is one like x or $\sin x$ for which the values of $f(x)$ and $f(-x)$ are negatives of each other. Thus, by definition

$$f(x) \text{ is even if } \ f(-x) = f(x)$$

$$f(x) \text{ is odd if } \ f(-x) \neq f(x)$$

Rules for obtaining the product of functions are as follows:

1) even function × even function
   = even function
2) odd function × odd function
   = even function
3) odd function × even function
   = odd function

Some functions are even, some are odd and some (for example e^x) are neither. However, any function can be written as the sum of an even function and an odd function.

THE ERROR FUNCTION

The error function is the area under a part of the curve described by $y = e^{-x^2}$. The error function is defined as

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt$$

Following are several useful facts about the error function:

1) Error function is odd; that is,
   $erf(-x) = -erf(x)$
2) $erf(\infty)$ can be evaluated as follows

$$erf(\infty) = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-t^2}\, dt = \frac{2}{\sqrt{\pi}}\, \tfrac{1}{2}\sqrt{(\tfrac{1}{2})} = \frac{2}{\sqrt{\pi}}\, \tfrac{1}{2}\sqrt{\pi} = 1$$

3) For very small values of x, $erf(x)$ can be evaluated by expanding e^{-t^2} in a power series and integrating term by term.

CHAPTER 15

Orbital Symmetry Conservation in Chemical Reactions

"Quantum mechanics can be used to predict the feasibility of a certain class of reactions e.g., electrocyclic reactions. This is governed by Woodward-Hoffmann symmetry conservation rule. It is intended to discuss this aspect of quantum mechanics in this chapter. Before we discuss a specific example, we will make a few comments on the symmetry of orbitals."

The wave function for the π orbital of ethylene has no nodes, whereas the wave function for the π^* orbital has one node.

The π orbital of ethylene has a plane of symmetry σ which bisects the molecule and is perpendicular to the molecular plane. The π^* orbital has a two-fold symmetry axis C_2 in the plane of the molecule, perpendicular to the carbon-carbon bond and bisecting the molecule.

It should be noted that π orbital does not possess C_2 axis of symmetry as defined above for π^* and similarily π^* orbital does not have the plane of symmetry σ. It is obvious that the two orbitals would transform differently on application of the symmetry operations of σ and C_2. We have seen earlier that *an orbital is symmetric* with respect to a symmetry operation if application of the symmetry operation produces an identity and antisymmetric if it does not π^* and π orbitals are antisymmetric (A) and symmetric (S) with respect to symmetry operation σ whereas these are symmetric and antisymmetric respectively with respect to C_2 operation. The results can be briefly summarised as follows:

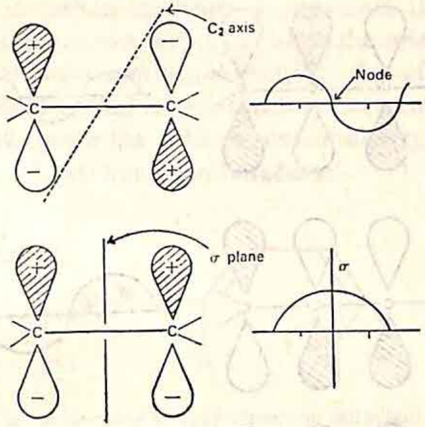


Fig. 15.1. Orbital representation.

	Symmetry element	
	σ	C_2
π^*	Antisymmetric (*A*)	Symmetric (*S*)
π	Symmetric (*S*)	Antisymmetric (*A*)

We can similarly examine the symmetry characters of orbitals of butadienes with respect to σ and C_2 operations. The four molecular orbitals of butadienes* may be represented as in Fig. 15.2.

The result of the symmetry operations with respect to σ and C_2 would be as follows

	σ	C_2
ψ_4	*A*	*S*
ψ_3	*S*	*A*
ψ_2	*A*	*S*
ψ_1	*S*	*A*

We shall now consider the symmetry control of Electrocyclic Reactions.

We consider the conversion of cyclobutene to butadiene i.e. from the view-point of symmetry conservation rule:

According to orbital symmetry conservation rule, the ground state

---

* (Cf. Fig. 10.3).

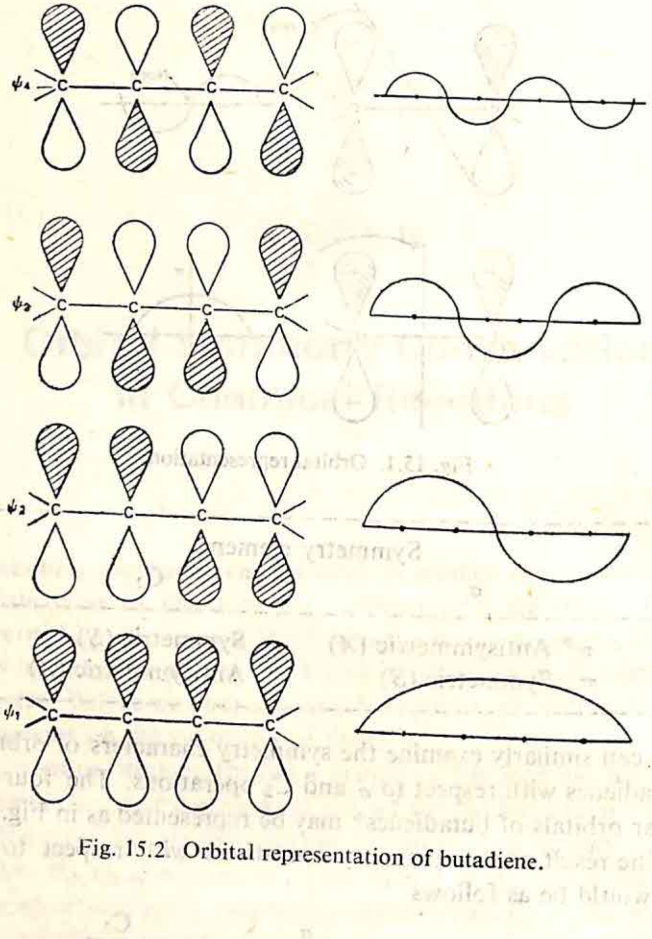


Fig. 15.2 Orbital representation of butadiene.

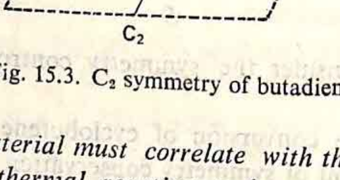


Fig. 15.3. C_2 symmetry of butadiene.

of the starting material must correlate with the ground state of the product for a thermal reaction to be symmetry allowed, the first excited state of the starting material must correlate with the first excited state of the product for a photochemical reaction to *be allowed.* Thus the orbital symmetry is conserved throughout. In a concerted reaction, a symmetric orbital in the starting material must transform into a symmetric orbital in the product and that an antisymmetric orbital must transform into an antisymmetric orbital. Following are the orbitals which undergo changes during conversion of cyclobutene to butadiene.

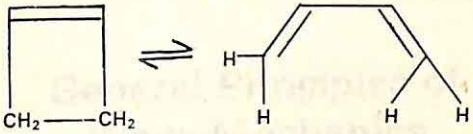


Fig. 15.4. Conversion of cyclobutene to butadiene.

Cyclobutene	Symmetry	Butadiene	Symmetry character
σ^*	*A*	ψ_4	*A*
π^*	*A*	ψ_3	*S*
π	*S*	ψ_2	*A*
σ	*S*	ψ_1	*S*

It is obvious that both the molecules have the plane of symmetry σ so that orbital symmetry is maintained throughout the reaction. Correlations of the orbitals is demonstrated in Fig. 15.5.

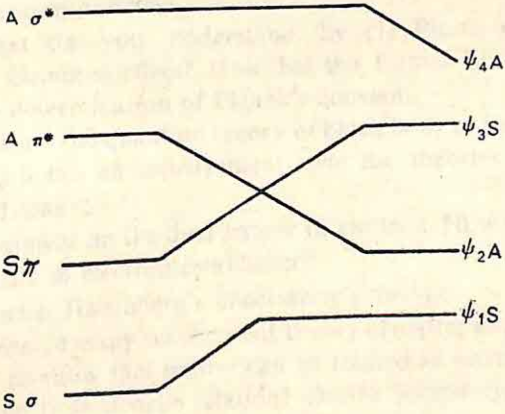


Fig. 15.5. Conservation of orbital symmetry.

The orbitals connected by the lines transform into each other. The cyclobutene ground state $\sigma^2 \pi^2$ correlates with a doubly excited state $\psi_1^2 \psi_3^2$ of butadiene. This is not allowed by symmetry conservation rule. However, the first excited state of cyclobutene $\sigma^2 \pi\pi^*$ correlates with the first excited state of butadiene $\psi_1^2 \psi_2 \psi_3$. According to symmetry conservation rule, the disrotatory process is photochemically allowed in either direction.

PROBLEMS

General Principles of Wave Mechanics

1. Give a brief account of Planck's quantum theory. How is the average energy of an oscillator calculated? Derive Einstein's expression for the specific heat at low temperatures and discuss its limitations.
2. What is photo electric effect? How is threshold potential measured? Give the theory of phenomena. Describe an experiment for the determination of Planck constant.
3. Discuss Bohr model of hydrogen atom. Deduce an expression for the energy levels. Explain the significance of four quantum numbers.
4. What do you understand by (1) Photo electric effect (2) Compton effect? How has the former been utilised for the determination of Planck's constant.
5. Discuss the quantum theory of black body radiation. In what way is this an improvement over the theories of Rayleigh and Jeans?
6. Comment on the dual nature of electron. How was the wave nature of electron established?
7. Discuss Heisinberg's uncertainty principle.
8. Write an essay on the dual theory of matter and give evidences to show that matter can be treated as waves.
9. What is de Broglie relation? Derive Schrödinger wave equation for hydrogen atom.

10. Write down Schrödinger wave equation and explain various terms.
11. Obtain the solution of Schrödinger equation for free particle moving in a box. Show that the spacing between the levels is greater where (i) the mass of the particle is smaller and (ii) size of the box is smaller.
12. Give an account of wave mechanical theory of covalence. What is understood by resonance?
13. Solve the Schrödinger equation for a particle in a rectangular three dimensional box. Comment on the use of this model in explaining the spectra of certain specific molecules.
14. Taking the case of linear harmonic oscillator, show that the quantisation of energy of dynamical system follows as a necessary consequence of obtaining acceptable solutions of its Schrödinger equation.
15. Give a solution of Schrödinger equation for a linear harmonic oscillator.
16. Give the outline of:
    a) Perturbation method
    b) Variation method
17. Calculate the wave length of (a) proton (b) an electron accelerated through a potential difference of 1 meV.

    Hint: Any particle of mass m moving with a velocity v has associated with it a wave length

    $$\lambda = \frac{h}{mv}$$

    A charged particle which has been accelerated through a potential difference V, has kinetic energy equal to

    $$\tfrac{1}{2}\, mv^2 = \frac{1}{300} \cdot e.V.$$

    e = electronic charge, V = potential difference, Factor of 300 arises in the conversion of units. Thus combining the above two equations:

    $$\lambda = \frac{300.h}{\sqrt{2m\, e.V.}}$$

18. For a particle of mass 9×10^{-28} gm confined to one-dimensional box 100 Å long, calculate the number of energy levels lying between 9 and 10 eV.

Solution

The allowed energy levels of a free particle of mass m confined to a one-dimensional box of size a are given by:

$$E_n = \frac{n^2\,h^2}{8ma^2} \text{ where } n = 1, 2, 3 \dots \text{ etc.}$$

or

$$n^2 = \frac{8ma^2}{h^2}\,E_n$$

number of energy levels between energy E_{n1} and E_{n2} would then be:

$$n_1 - n_2 = \left[\frac{8ma^2}{h^2}\right]^{\frac{1}{2}} \cdot (E_{n1}{}^{\frac{1}{2}} - E_{n2}{}^{\frac{1}{2}})$$

$$E_{n1} = 10\times1.6\times10^{-12} \text{ ergs} \qquad m = 9\times10^{-28}$$

$$a = 10^{-6} \text{ cm}$$

$$h = 6.6\times10^{-27}$$

$$E_{n2} = 9\times1.6\times10^{-12} \text{ ergs}$$

then $n_1 - n_2 = 3$.

19. Calculate the minimum uncertainty in the position or velocity for following cases:

a) an automobile moving with 60 ± 0.001 km/hr (mass = 1000 kg).

b) A bullet whose position at time t is known to ± 0.01 mm (mass = 10 gm).

c) Hydrogen atom whose velocity is known to ± 1 cm/sec.

d) An electron whose position is known to ± 1.0 Å.

Hint: Uncertainty principle in position and velocity can be written as:

$$\Delta \times \Delta\, v_x \sim h/m.$$

where m is the mass of the particle

20. A snail of mass 1 gm is travelling at a velocity of 0.1 mm/sec. What is the uncertainty in position?

21. Show that when $n_x = n_y = n_z = 0$ for a particle in a box, we have an infinitily large; wavelength or uncertainty in position.

Solution

The energy eigenvalues for a particle in cubical box of size a are given as:

$$E = \frac{h^2}{8\,ma^2}(n_x^2 + n_y^2 + n_z^2)$$

Where n_x, n_y and n_z are quantum numbers. In the present case $n_x = n_y = n_z = 0$, therefore $E = 0$.

But $E = \frac{p^2}{2\,m}$ where p = momentum; then p is also equal to zero. From de Broglie relation $\lambda = h/p$

since $$p = 0, \quad \lambda = \infty$$

and from uncertainty principle

$$\Delta x = \frac{h}{p} = \infty$$

22. What is the degeneracy of the level for which

a) $E = \frac{14\,h^2}{8\,ma^2}$

b) $E = \frac{27\,h^2}{8\,ma^2}$

and what are the values of n_x, n_y and n_z.

Solution

a) $n_x^2 + n_y^2 + n_z^2 = 14$ the possible arrangement could be

n_x	n_y	n_z
3	1	2
2	1	3
3	2	1
1	2	3
1	3	2
2	3	1

Hence degeneracy is 6.

b) $n_x = n_y = n_z = 3.$

23. For a free particle in one dimensional box of length a, ψ function for ground state could be assumed to be $cx\,(x-a)$, where c is a constant. Show that this satisfies the boundary condition. Calculate E for ground state using variational method.

Solution

The trial wave function $= cx(x-a)$. The boundary condition for one dimensional box are

$$\psi(v) = (0) \text{ at } x = 0 \quad \text{and } \psi(a) = 0 \quad \text{at } x = a.$$

Thus ψ satisfies these boundary conditions

$$\text{The energy} \quad E = \frac{\int_0^a \psi\, H\, \psi\, dx}{\int_0^a \psi^*\, \psi\, dx}$$

$$\text{Now} \int_0^a \psi\, H\psi\, dx = \int_0^a x(x-a)\left(-\frac{h^2}{8\pi^2 m}\cdot\frac{d^2}{dx^2}\right) x(x-a)\, dx$$

$$= -\frac{h^2}{8\pi^2 m}\cdot\int_0^a x(x-a)\cdot 2\, dx$$

$$= -\frac{h^2}{4\pi^2 m}\int_0^a x(x-a)\, dx = \frac{h^2}{4\pi^2 m}\cdot$$

$$\left(-\frac{1}{6}\right) a^3 = \frac{h^2 a^3}{24\pi^2 m}.$$

$$\text{Further,} \quad \int_0^a \psi^*\, \psi\, dx = \int_0^a x^2(x-a)^2\, dx = \frac{a^5}{30}$$

$$\text{Therefore} \quad E = \frac{h^2 a^3}{24\pi^2 m}\cdot\frac{30}{a^5} = \frac{5\, h^2}{4\pi^2\, ma^2}.$$

It should be noted that for 1^D case when true wave function is

$\psi = A \sin \dfrac{n\pi x}{a}$, the energy of ground state

$$E = \frac{h^2}{8\, ma^2}$$

Thus the difference in the ground state energy using true wave function and approximate w.f. $\simeq 1.3\%$.

24. Consider a particle in one-dimensional potential well. The potential energy is given by $V(x) = c.\dfrac{x}{a}$. Estimate the 1st order perturbation energy of the system.

Solution

For unperturbed system the Hamiltonian operator H° is given as:

$$H^\circ = -\frac{h^2}{8\ ^2m}\cdot\frac{d^2}{dx^2}\cdot \text{ when } V(0) = 0.$$

and the unperturbed wave function are $\psi = A\sin\dfrac{n\pi x}{a}$

$$= A\sin\frac{n\pi x}{a}\cdot \quad \text{where } A^2 = \frac{2}{a}$$

from normalisation. Further,

$$E^\circ = \frac{n^2 h^2}{8ma^2}$$

The Hamiltonion operator H, for perturbed system is given as:

$$H = H^\circ + H'$$

Where H' is due to perturbation, or

$$H = -\frac{h^2}{8\pi^2 m}\cdot\frac{d^2}{dx^2} + c\left(\frac{x}{a}\right)$$

The energy of the perturbed state $E = E^\circ + E'$

$$\text{where } E' = \frac{\int_0^a A\cdot\sin\dfrac{n\pi x}{a}\cdot\left(c\dfrac{x}{a}\right)\cdot A\sin\dfrac{n\pi x}{a}\cdot dx.}{A^2\sin^2\dfrac{n\pi x}{a}\,dx}$$

$$= \frac{c}{a}\int_0^a x\cdot\sin^2\frac{n\pi x}{a}\cdot dx.$$

$$= \frac{c}{2}.$$

therefore $E = E^\circ + \dfrac{c}{2}$ or $\dfrac{n^2h^2}{8ma^2} + \dfrac{c}{2}$

25. Show that functions

a) $\psi = c \exp(ax)$, where a is a constant

b) $\psi = 8 \exp(5x)$

are the eigen functions of the operator (d/dx). Calculate the eigen value.

26. Show that the function $\psi = x \exp(-ax^2)$ is an eigen function of the operator (d^2/dx^2). What is its eigenvalue?

27. Obtain the Schrödinger equation for a free particle in a ring. Deduce expression for energy and wave function. How can this solution be applied to benzene?

Quantum Mechanics of Atoms

1. Give the wave mechanical treatment of hydrogen atom.
2. Discuss the perturbation treatment of the ground state of Helium atom. How does the exchange degeneracy arise? How can you prove that total wave function must be anti-symmetric to inter-change of electrons?
3. Calculate the Bohr Radius of He^+ and Li^{2+}.

Hint: According to Bohr theory radius of *n*th orbit of an electron of mass *m*, moving around a nucleus of charge $Z.e$ is given by:

$$r_n = \frac{h^2 n^2}{4\pi^2 me^2 Z} \text{ when } n = 1, 2, 3 \ldots$$

for 1st Bohr orbit

$$r = \frac{h^2}{4\pi^2 me^2 Z}$$

He^+ and Li^{2+} are hydrogen like atoms since they also have only one electron moving around charge $2e$ and $3e$ respectively.

4. A positive and negative electron can form a short lived complex called positronium. Assume that the Bohr theory of the hydrogen atom could be applied to positronium, calculate the:
   a) Energy difference between its ground and first excited state.
   b) Bohr radius.

Solution

According to Bohr theory the radius and energy of the *n*th orbit is given by:

$$E_n = -\frac{2\pi^2 \mu Z^2 e^4}{h^2} \cdot \frac{1}{n^2} \quad \text{and} \quad r_n = \frac{n^2 h^2}{4\pi^2 \mu e^2 Z}$$

where μ is the reduced mass of the system and is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

In case of positronium, an electron moves around a position, both have same mass equal to the mass of an electron m, therefore the reduced mass $\mu = \frac{m}{2}$ and $Z = 1$. Thus

$$E_1 = -\frac{2\pi^2 me^4}{2h^2}, \quad r_1 = +\frac{2h^2}{4\pi^2 me^2} = \frac{h^2}{2\pi^2 me^2}$$

and

$$E_2 = -\frac{2\pi^2 me^4}{2h^2 \times 2^2}; \quad E_1 - E_2 = -\frac{\pi^2 me^4}{h^2}\left[1 - \frac{1}{4}\right]$$

$$= -\frac{3\pi^2 me^4}{4h^2}$$

The values of E compared to hydrogen atom is just half and the Bohr radius is just the double.

5. Calculate the following for positronium:
   a) Ionisation energy,
   b) Energy level of the first excited state, and
   c) Radius a_0 in the ground state.

   Hint: for ionisation energy $n_1 = 1$ and $n_2 = \infty$. Use the expressions for energy and radius given in problem No. 4.

6. Show that the ψ_{1s} function for hydrogen atom is orthogonal to ψ_{2s} and ψ_{2p} functions.

Solution

$$\psi_{1s} \text{ for hydrogen} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3}\left(2 - \frac{1}{a_0}\right) e^{-r/2a_0}$$

Two wave functions are said to be orthogonal if

$$\int_0^\infty \psi_1^* \psi_2 \, d\tau = 0$$

Therefore,

$$\int_0^\infty \frac{1}{4\sqrt{2\pi}}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^3\left(2-\frac{r}{a_0}\right)e^{-3r/2a_0}\,4\pi r^2\,dr$$

should be Zero

$$=\frac{1}{\sqrt{2}}\left(\frac{1}{a_0}\right)^3\int_0^\infty r^2\left(2-\frac{r}{a_0}\right)e^{-3r/2a_0}\,dr = 0$$

the integral can be evaluated by using the integral

$$\int_0^\infty x^{n+1}\,e^{-ax}\,dx = \frac{n\,!}{a^{n+1}}$$

7. Consider an electron in a hydrogen like $2p_z$ orbital, what is the relative probability density that it will be at $\theta = \frac{\pi}{2}$ and $\theta = 45°$ (i.e. on the X-axis and 45° to it).

Solution

$$\psi 2p_z = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\cos\theta$$

the probability density $= \psi^2_{2p_z}$

$$=\frac{1}{32\pi}\left(\frac{1}{a_0}\right)^5 r^2\,e^{-r/a_0}\cos^2\theta$$

when $\theta = 90°$ or $\pi/2$ $\psi^2_{2p_z} = 0$

when $\theta = \pi/4$ $\psi^2_{2p_z} = \dfrac{1}{64\pi}\dfrac{1}{a_0{}5}r^2\,e^{-r/a_0}$

8. The wave function for the electron in the ground state of hydrogen atom is $\psi_{1s} = (\pi a_0)^{-1/2}\,e^{-r/a_0}$ where a_0 is the radius of the Bohr orbit. Calculate the probability that the electron will be found some where between 0.9 and 1.1. What is the probability that this electron will be beyond $2a_0$?

Solution

The probability that the electron will be found between 0.9

and 1.1 $= \int_{0.9a_0}^{1.1a_0} \psi_{1s}^2 \, 4\pi r^2 \, dr$

$$= \frac{4}{a_0^3} \int_{0.9a_0}^{1.1a_0} r^2 \exp\left(-\frac{Zr}{a_0}\right) dr$$

Put $\frac{Zr}{a_0} = x;$ hence $dr = \frac{a_0}{2} dx$

Hence, the probability $= \frac{1}{2} \int_{1.8}^{2.2} x^2 e^{-x} \, dx$

$$= \tfrac{1}{2} \left[-x^2 e^{-x} - 2x e^{-x} - 2e^{-x}\right]_{1.8}^{2.2}$$

$$= \tfrac{1}{2} e^{-x} (x^2 + 2x + 2)_{2.2}^{1.8}$$

$$= \tfrac{1}{2} (8.84 \times 1653 - 11.24 \times 1108)$$

$$= \tfrac{1}{2} (1.46 - 1.245) = \frac{\cdot 2146}{2}$$

$$= 0.1073 \text{ ANS.}$$

Probability that the electron will be found beyond $2a_0$

$$= \frac{4}{a_0^3} \int_{2a_0}^{\infty} r^2 e^{-2r/a_0} \, dr \text{ as done above}$$

$$= \tfrac{1}{2} \left[+ e^{-x} (x^2 + 2x + 2)\right]_{\infty}^{4}$$

$$= \tfrac{1}{2} e^{-4} (16 + 8 + 2) = 13 \times e^{-4} = 0.238 \text{ ANS.}$$

9. Show that the hydrogen wavefunctions for $l = 1$ have maximum value along the direction of the cartesian axes.

Solution

i) $\psi 2p_z = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$

Condition for maximum $= \frac{d\psi}{d\theta} = 0$

Differentiating w.r.t. θ we get

$$\frac{d\psi}{d\theta} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0}\, e^{-r/2a_0}\,(-\sin\theta) = 0.$$

Therefore $\theta = 0$ or π. Hence maxima is along Z-axis.

ii) Similarly $\psi 2p_x = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0}\, e^{-r/2a_0}$

$\sin\theta\cos\phi$

$$\frac{d\psi}{d\theta} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0}\, e^{-r/2a_0}\cos\phi\cos\theta = 0$$

therefore $\theta = \frac{\pi}{2}$ or $3\pi/2$.

Hence maxima is along X-axis.

iii) For $\psi 2p_y = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0}\, e^{-r/2a_0}\sin\theta\sin\phi$.

the maxima would be along Y-axis.

10. Find the direction in cartesian coordinates in which the angular wave functions of hydrogen for $l = 2$ have maxima.

Hint: The angular w.f. for $l = 2$ are

$$\frac{\sqrt{15}}{4}\frac{1}{\sqrt{3\pi}}(3\cos^2\theta - 1)$$

$$\left(\frac{15}{16\pi}\right)^{1/2}\sin 2\theta\cos\phi$$

$$\left(\frac{15}{16\pi}\right)^{1/2}\sin 2\theta\sin\phi$$

$$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$$

$$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin^2\phi$$

condition for maxima $= \frac{d\psi}{d\theta} = 0$

ANS: $\left(0, \pi/2, \pi \text{ and } \frac{3\pi}{2}\right)$, $\frac{\pi}{4}$ and $\frac{3\pi}{4}$, $\frac{\pi}{4}$ and $\frac{3\pi}{4}$, 0, $\frac{\pi}{2}$, π and $\frac{3\pi}{2}$

11. The 1s wave function for hydrogen atom is:

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

Compute the probability of electron being at

a) $r = 0$ and $r = a_0/2$

b) $r = 0$ and $r = a_0$

c) $r = 0$ and $r = 3/2\, a_0$

Hint: Same as 8.

12. Show that for the ground state of hydrogen atom, the quantum mechanical treatment requires that the most probable value of the function $4\pi\, r^2\, \psi^2$ related to the probability is obtained at the distance r from the nuclei equal to Bohr radius a_0.

$$\text{Function } P = 4\pi\, r^2 \exp\left(\frac{-2r}{a_0}\right)$$

The function would be maximum when $\dfrac{dp}{dr} = 0$

i.e. when $4\pi\, 2r \exp\left(\dfrac{-2r}{a_0}\right) - 4\pi\, r^2 \dfrac{2}{a_0} \exp\left(\dfrac{-2r}{a_0}\right) = 0$

i.e. when $r = a_0$

13. a) What would be the value of ψ (1s) at $r = 0$

b) What would be the value of ψ (2s) when $Zr = 2a_0$

c) What would be the value of $\psi 2s$ at $\theta = \pi/2$

$\psi 2p_x$ when $\phi = \pi/2$

$\psi 2p_z$ when $\phi = \pi/2$

d) Calculate ratio of $\dfrac{\psi_{2p_x}^2}{\psi_{2p_y}^2}$ when $\theta = \pi$ and $\dfrac{\pi}{3}$

14. Show that ψ_{1s} is a continuous and single valued function.

15. Write the Schrödinger wave equation for the following atom:

a) He, Li^+

b) multi electron atoms.

explain the various interaction terms.

16. Plot the probability distribution function ψ_{2p}^2 as a function of θ given that:

$\psi_{2p}^2 = \text{constant}\ (1 + \cos 2\theta)$

Solution

values of θ and $\cos 2\theta$ are given below

θ	15°	30°	60°	90°	120°	150°	180°	210°	270°	300°	360°
$\cos 2\theta$	0.866	0.5	−0.5	−1	−0.5	0.5	1.0	0.5	−1.0	−0.5	1.0

17. Write Hamiltonian operator and ψ-function of Li^+ atom taking into account the spin of all the electrons:

Solution

$$H = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - 3e^2\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right) + e^2\left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right)$$

where r_1, r_2 and r_3 are the distances of the electrons from the nuclei and r_{12}, r_{13} and r_{23} are the inter-electronic distances. ψ is written as Slater determinant form for n electrons

$$\psi = \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_{1s}^{(1)}\,\alpha(1) & \varphi_{1s}^{(1)}\,\alpha(2) & \cdots & \varphi_{1s}(n)\,\alpha(n) \\ \varphi_{1s}^{(1)}\,\beta(1) & \varphi_{1s}(2)\,\beta(2) & \cdots & \varphi_{1s}(n)\,\beta(n) \\ \varphi_{2s}(1)\,\beta(1) & \varphi_{2s}(2)\,\alpha(2) & \cdots & \phi_{2s}(n)\,\alpha(n) \\ \phi_{2s}(1)\,\beta(1) & \phi_{2s}(2)\,\beta(2) & & \phi_{2s}(n)\,\beta(n) \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}$$

Therefore for Li atom $n = 3$

$$\psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \phi_{1s}(1)\,\alpha(1) & \phi_{1s}(2)\,\alpha(2) & \phi_{1s}(3)\,\alpha(3) \\ \phi_{1s}(1)\,\beta(1) & \phi_{1s}(2)\,\beta(2) & \phi_{1s}(3)\,\beta(3) \\ \phi_{2s}(1)\,\alpha(1) & \phi_{2s}(2)\,\alpha(2) & \phi_{2s}(3)\,\alpha(3) \\ \phi_{2s}(1)\,\beta(1) & \phi_{2s}(2)\,\beta(2) & \phi_{2s}(3)\,\beta(3) \end{vmatrix}\, 2s^1$$

18. Write H and ψ for He atom

$$H = \frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - 2e^2\left(\frac{1}{r_1} + \frac{1}{1_2}\right) + \frac{e^2}{r_{12}}$$

$$\psi = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_{1s}(1)\,\alpha(1) & \phi_{1s}(2)\,\alpha(2) \\ \phi_{1s}(1)\,\beta(1) & \phi_{1s}(2)\,\beta(2) \end{vmatrix}$$

Quantum Mechanics of Molecules

1. Explain the difference between:
   a) Valence bond approach.
   b) Molecular orbital approach.

   Discuss the wave mechanics of hydrogen molecule in this context.

   The binding energy of N_2^+ is 6.35 and that of N_2 7.38 eV. whereas the binding energy of O_2^+ is 6.48 and that of O_2 5.08 eV. How would you explain this on the basis of molecular orbital theory?
2. Give the wave mechanical treatment of hydrogen molecule ion. What is understood by bonding, and antibonding molecular orbitals.
3. Give an account of wave mechanical theory of covalence, what is understood by resonance.
4. Construct the *sp* and *sp*^{2} hybrid orbitals by combining atomic orbitals. Evaluate the coefficients, by using normalisation condition and orthogonality theorem. Trace the angular variation of such orbitals.
5. Give the molecular treatment of hydrogen molecule ion. Discuss the electronic energy level diagrams.
6. Outline the wave mechanical treatment of hydrogen molecule and hydrogen molecule ion. Discuss the significance of symmetric and antisymmetric solutions. Briefly discuss the relative merits of valence bond and molecular orbital approach.
7. Give the valence bond (Heitler-London) treatment of hydrogen molecule. Explain Coulomb and Resonance integrals.
8. Give an outline of molecular orbital treatment of diatomic molecules.

9. Give an account of the M.O. theory of simple diatomic molecules. Prepare a table summarising M.O. configuration, and bond orders for the molecules N_2, O_2 and NO.
10. Discuss the M.O. treatment of benzene. How is resonance energy calculated?
11. Outline the LCAO. M.O. theory of benzene. Evaluate the energies of molecular orbitals and hence calculate the resonance energy.
12. Show that the electron density at all the carbon atoms is unity for butadiene.
    Calculate the bond order for ethylene.
13. Discuss the M.O. theory of butadiene molecule.
14. How are the following determined.
    1) Delocalisation energy of cyclobutadiene. i.e.
    2) Wave functions for naphthalene molecule using group theory.
15. If ψ_1 and ψ_2 are wave functions for a degenerate energy state E, prove that any linear combination $C_1 \psi_1 + C_2 \psi_2$ is also a wave function.

Solution

The wave equation can be written as:

$$\frac{h^2}{8\pi^2 m}\frac{d^2 \psi}{dx^2} + (E-V)\psi = 0$$

ψ_1 and ψ_2 are wave function for the energy state E, then

$$\frac{h^2}{8\pi^2 m}\frac{d^2 \psi_1}{dx^2} + (E-V)\psi_1 = 0 \qquad (1)$$

and
$$\frac{h^2}{8\pi^2 m}\frac{d^2 \psi_2}{dx^2} + (E-V)\psi_2 = 0 \qquad (2)$$

multiply equations (1) and (2) by constants C_1 and C_2 respectively and adding we get:

$$\frac{h^2}{8\pi^2 m}\left(\frac{d^2 C_1 \psi_1}{dx^2} + \frac{d^2 C_2 \psi_2}{dx^2}\right) + (E-V)(C_1 \psi_1 + C_2 \psi_2) = 0$$

or
$$\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}(C_1 \psi_1 + C_2 \psi_2) + (E-V)(C_1 \psi_1 + C_2 \psi_2) = 0$$

It means $C_1 \psi_1 + C_2 \psi_2$ is also an eigenfunction of energy state E.

16. Describe the molecular orbitals that would be used in the molecules HeH^+, LiH, CO, CN.

Solution

In M.O. method the electrons outside closed shell, (valence electrons) make a contribution to the binding energy of a molecule. Therefore, for a molecule like LiH. The valence electron is $2s^1$ and H $= 1s^1$.

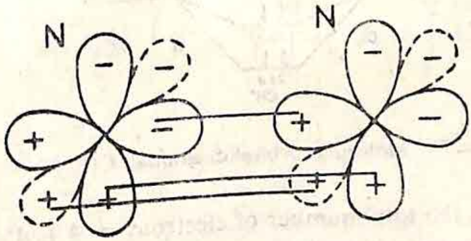
Therefore,
$$\psi\text{LiH} = \psi_{2s}(\text{Li}) + \psi_{1s}(\text{H})$$
$$\psi\text{HeH}^+ = \psi_{1s}(\text{He}^+) + \psi_{1s}(\text{H})$$
$$\psi\text{CO} = \psi_{2p}(\text{C}) + \psi_{2p}(\text{O})$$
$$\psi\text{CN} = \psi_{2p}(\text{C}) + \psi_{2p}(\text{N})$$

17. In terms of the valence bond and molecular orbital theories describe and compare:

a) N_2 and C_2H_2
b) NO, HF, H_2O, NH_3 and CH_4

Solution

a) Valence bond



V.B. model of N_2.

M.O.

$N_2 = 1s\,\sigma^2,\ 1s\,\sigma^{*2},\ 2s\,\sigma^2,\ 2s\,\sigma^{*2},\ 2p\,\sigma^2,\ 2p\,\pi^4$ one sigma and 2π bonds.

$C_2H_2 = 1s\,\sigma^2\ 1s\,\sigma^{2*},\ 2s\ \sigma^2_{C-H},\ 2s\,\sigma^{2*}_{C-H},\ 2p\,\sigma^2_{C-C}\ 2p\,\pi^4_{C-C}$

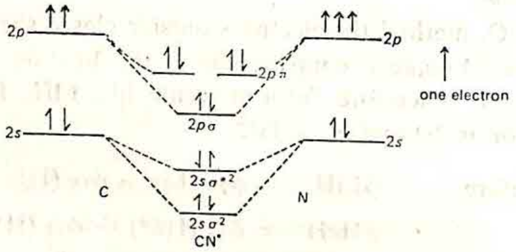
18. By means of correlation diagram with added electrons describe the free radicals $\dot{C}N$, $C\dot{H}$, $\dot{C}_2$. Estimate relative internuclear distance from the net number of bonding electrons.

Solution

$C\dot{N}$, the total number of electrons outside closed shells

$$= 4 + 5 + 1 = 10$$

M.O. correlation diagram would be:



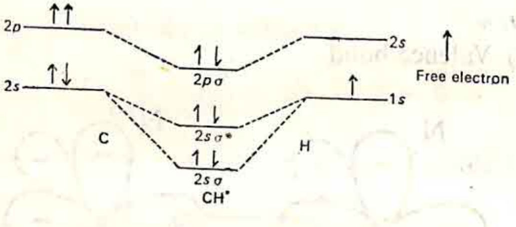
Molecular orbital diagram of $C\dot{N}$

Bond order = 3.

For CH, total number of electron outside closed shell

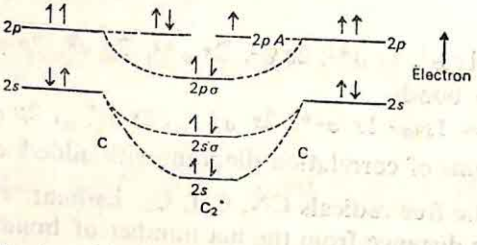
$$= 4 + 1 + 1 = 6.$$

M.O. diagram would be as shown as follows



Molecular orbital diagram of $C\dot{H}$

For $\dot{C}_2$, the total number of electrons = 4 + 4 + 1 = 9 and M.O. diagram is as shown



Molecular orbital energy diagram of $\dot{C}_2$ free radical

Bond order = 2.5
then the internuclear distance would increase in the order

$$\mathrm{C\dot{N}} < \mathrm{\dot{C}} < \mathrm{C\dot{H}}$$

19. If sp^2 hybridised normalised orbitals are orthonormal and given as:

$$\psi_1 = \frac{1}{\sqrt{3}}\, s + \frac{2}{\sqrt{3}}\, p_x$$

$$\psi_2 = \frac{1}{\sqrt{3}}\, s + \frac{1}{\sqrt{6}}\, p_x + \frac{1}{\sqrt{2}}\, p_y$$

$$\psi_3 = \frac{1}{\sqrt{3}}\, s + C_2\, p_x + C_3\, p_y$$

Find the value of C_2 and C_3.

Solution

These orbitals are orthgonal. It means they must satisfy the condition

$$\int_0^\infty \psi_1\, \psi_3\, d\tau = 0 \quad \text{and} \quad \int_0^\infty \psi_2\, \psi_3\, d\tau = 0$$

also we know that $\int_0^\infty \psi_s^2\, d\tau = \int_0^\infty \psi_{p_x}^2\, d\tau = \int_0^\infty \psi_{2p_y}^2\, d\tau = 1$

and $\int_0^\infty \psi_e\, \psi_{p_x}\, d\tau = \int_0^\infty \psi_s\, \psi_{p_y}\, d\tau = \int_0^\infty \psi_{p_z} \int \psi_{p_y}\, d\tau = 0$

then applying the condition of orthogonality

$$\Big[\, \psi_1\, \psi_3\, d\tau = 0 = \int_0^\infty \left(\frac{1}{\sqrt{3}}\, S + \frac{2}{\sqrt{3}}\, p_x \right)$$

$$\left(\frac{1}{\sqrt{3}}\, s + C_2 p_x + C_3 p_y \right) d\tau$$

$$0 = \int_0^\infty \Bigg({}^{1}\, s^2 + \frac{C_2}{\sqrt{3}}\, s \cdot p_x + \frac{C_3}{\sqrt{3}}\, s \cdot p_y + \frac{\sqrt{2}}{3}$$

$$s \cdot p_x + C_2 \frac{2}{3} p_x^2 + C_3 \sqrt{\frac{2}{3}} p_x p_y \Big) d\tau$$

$$0 = \frac{1}{3} + C_2 \sqrt{\frac{2}{3}} \quad \text{or } C_2 = \frac{1}{\sqrt{6}}$$

Again

$$\int_0^\infty \psi_2 \psi_3 \, d\tau = 0 = \int_0^\infty \left(\frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y \right)$$

$$\left(\frac{1}{\sqrt{3}} s + C_2 p_x + C_3 p_y \right) d\tau$$

$$0 = \int_0^\infty \Big(\frac{1}{3} s^2 + \frac{\cdot C_2}{\sqrt{3}} s p_x + \frac{1}{\sqrt{3}} C_3 p_y^2 -$$

$$\frac{1}{\sqrt{1s}} s p_x - \frac{C_2}{\sqrt{6}} p_x^2 - \frac{C_3}{\sqrt{6}} p_x p_y +$$

$$\frac{1}{\sqrt{6}} s p_y + \frac{C_2}{\sqrt{2}} p_x p_y + \frac{C_2}{\sqrt{2}} p_y^2 \Big) d\tau$$

$$\frac{C_2}{\sqrt{6}} - \frac{C_3}{\sqrt{2}} = \frac{1}{3} \text{ and } C_3 = + \frac{\sqrt{2}}{6}$$

20. If the wave functions for two electrons are as follows:

$$\psi_1 = C_{11} \psi_s + C_{12} \psi_p$$

$$\psi_2 = C_{21} \psi_s + C_{22} \psi_p$$

and they are orthogonal, prove that

$$C_{11} C_{21} + C_{12} C_{22} = 0$$

Hint: apply the orthogonality condition and solve as example 18

21. Using molecular orbital theory explain the following:
- a) Hc_2 and Be_2 do not exist.
- b) O_2 is para magnetic while N_2 is not.
- c) N_2 molecule has one σ and two π-bonds.
- d) N_2 and CO have similar physical properties.
- e) O_2 is less state than O_2^+.

22. Draw energy level diagrams and write the electronic structure of H_2^+, H_2, He_2^+, Hc_2, Li_2, Bc_2, B_2, C_2

N_2, F, CO, C_6H_6, C_2H_2, CN^- and NO

23. When do the atomic orbitals interact to form a molecular orbitals?

24. What are the rules for filling M.O. of a molecule?

25. Explain the significance of M.O.

26. Given an explanation of the following on the basis of M.O. theory:

a) NO^+ and N_2 are both diamagnetic and have similar properties.

b) Both NO and NO^- are paramagnetic.

27. Which molecules among the following pairs have greater dissociation energy:

a) O_2 , O_2^- d) C_2 , C_2^-

b) Be_2 , Be_2^+ e) F_2 , F_2^+

c) B_2 , B_2^+ f) NO , NO^-

28. Differentiate between:
Atomic orbital, Hybrid A.O, M.O. and a hybrid M.O.

29. Predict whether (a) Li_2, and (b) Be_2 can exist.

30. Using HMO theory determine the energy of the following Allylic systems:

$$C_3H_5^+,\quad C_3H_5^{\cdot}\quad \text{and}\quad C_3H_5^-$$

Solution

The allylic system is:

$$\underset{1}{C}—\underset{2}{C}—\underset{3}{C}$$

The secular determinant for the system would be if;

$$\frac{\alpha - E}{\beta} = x$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

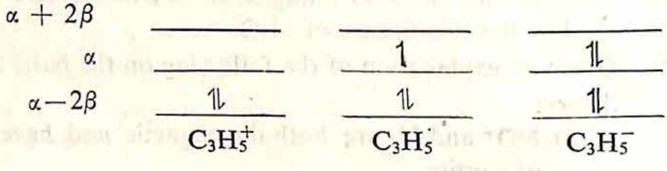
On solving the determinant:

$x^3 - 2x = 0$ then $x = 0$ and $x = \pm\sqrt{2}$

therefore energy levels

$$E_1 = \alpha + \sqrt{2}\,\beta,\ E_2 = \alpha \quad \text{and} \quad E_3 = \alpha - \sqrt{2}\,\beta$$

the energy level diagram for various allylic systems would then be as:



The total π-electron energy of cation $E_\pi^+ = 2\alpha + 2\sqrt{2}\,\beta$

For allylic anion $C_3H_5^-$ $= 2\,(\alpha + \sqrt{2}\,\beta) + 2\,(\alpha)$

$= 4\alpha + 2\sqrt{2}\,\beta$

and

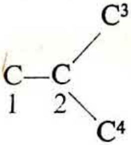
For allylic radical $C_3H_5^{\cdot}$ $= 2\,(\alpha + \sqrt{2}\,\beta) + \alpha$

$= 3\alpha + 2\sqrt{2}\,\beta$

31. Using HMO calculate the energy of Trimethylene methane and draw energy level diagram.

Solution

The Trimethyl methane is:



the secular determinant will be:

$$\begin{vmatrix} x & 1 & 1 & 1 \\ 1 & x & 0 & 0 \\ 1 & 0 & x & 0 \\ 1 & 0 & 0 & x \end{vmatrix} = 0$$

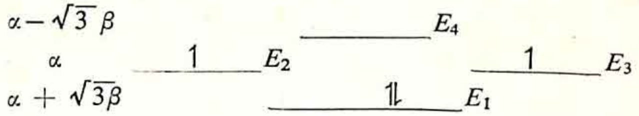
On solving the determinant we get

$$x^4 - 3x^2 = 0 \quad \text{thus } x = 0 \quad \text{and } x = \pm\sqrt{3}.$$

Hence,

$$E_1 = \alpha + \sqrt{3}\,\beta, \quad E_2 = E_3 = \alpha, \quad E_4 = \alpha - \sqrt{3}\,\beta$$

Therefore the energy level diagram will be:



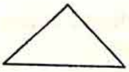
Two of the four available π-electrons are put as usual in the first energy level. The next level is two-fold degenerate. In such a case according to Hund's rule, one electron is placed in each level with unpaired spins.

$$\text{Total } \pi\text{-electron energy } E = 4\alpha + 2\sqrt{3}\beta$$

The parallel spins indicate that the compound is a *di* radical.

32. Using HMO theory obtain the total energy and the *DE* for the following network.

(a)



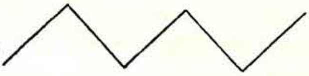
ANS. $x = -2, 1, 1$

$E_\pi^+ = 2\alpha + 4\beta,\ DE = 2\beta$

$E_\pi^\circ = 3\alpha + 3\beta \quad DE = \beta$

$E_\pi^- = 4\alpha + 2\beta \quad DE = 0$

(b)

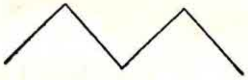


ANS. $x = \pm 1.802, \pm 1.247, \pm 0.445$

$E_\pi = 6\alpha + 6.988\beta,$

$DE = 0.988\beta$

(c)



ANS. $x = 0, \pm\sqrt{3}, \pm 1$

$E_\pi^+ = 4\alpha + 5.464\beta,$

$DE = 1.464\beta$

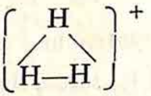
$E_\pi^\circ = 5\alpha + 5.464\beta,$

$DE = 1.464\ \beta$

$E_\pi^- = 6\alpha + 5.464\beta,$

$DE = 1.464\beta$

33. Calculate by LCAO M.O. method using SHMO theory, whether the linear $(H-H-H)^+$ or the triangular state



is more stable. Do the same for H_3 and H_3^-.

Solution

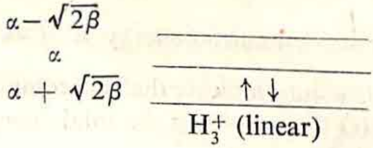
For linear H_3^+, the determinant will be:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

On solving $x^3 - 2x = 0$ then $x = \pm\sqrt{2}$ and $x = 0$

Thus $E_1 = \alpha + \sqrt{2\beta}$, $E_2 = \alpha$ and $E_3 = \alpha - \sqrt{2\beta}$

The energy level diagram will be:



$$\text{Total} \quad E = 2\alpha + 2\sqrt{2\beta}$$

For H_3, we have one more electron, hence $E = 3\alpha + 2\sqrt{2\beta}$ and H_3^-, it would be $4\alpha + 2\sqrt{2\beta}$

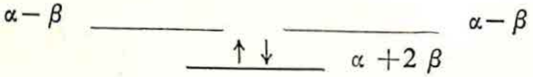
Proceeding in the same way for triangular H_3^+, the secular determinant will be:

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

so that $x^3 - 3x + 2 = 0$ or $x = \pm 1, 1$ and -2.

Thus $E = \alpha - 2\beta,\ \alpha - \beta,\ \alpha - \beta$

and the energy level diagram will then be



Total energy $E = 2\alpha + 4\beta$

For H_3 $E = 3\alpha + 3\beta$

and H_3^- $E = 4\alpha + 2\beta$

Thus since β is negative and α is positive.

i) Energy of H_3 is less than H_3^-, and

ii) Energy of H_3^+ is less than H_3.

34. Calculate the E_π of Benzene molecule and draw its energy level diagram.

ANS. $6\alpha + 8\beta$

35. Predict the aromaticity of C_6H_6.

Solution

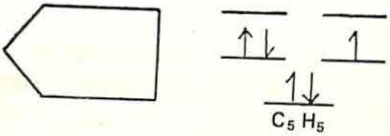
$n_\pi = 6$. According to $4m + 2$ rule with

$m = 1 \qquad n_\pi = 6.$

It is predicted to have extrastability resulting from resonance energy associated with aromatic compounds.

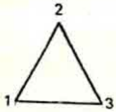
36. Draw energy level diagram of the ground state configuration of $C_5H_5^+$, $C_5H_5^{\cdot}$ and $C_5H_5^-$. Which is the most stable according to $4m + 2$ rule?

ANS. $C_5H_5^-$



37. Find the electron density for each of the following systems.

Cyclopropenyl



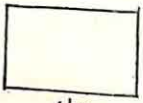
(a)

ANS.

Cation $q_1 = q_2 = q_3 = 0.677$

Anion $q_1 = q_2 = q_3 = 1.33$

Cyclobutadiane



(b)

ANS.

$q_1 = q_2 = q_3 = q_4 = 1$

38. The molecule ion HeH^+ is similar to H_2 in that there are only two orbital electrons

a) Would you expect the ionic character of HeH^+ to be greater or smaller than that of H_2?

b) Can the simple valence bond wave function for H_2 be used for HeH^+? Explain.

Solution

More ionic character because electrons will spend more time around He nucleus.

c) No. Since the two atoms are different, two ionic terms corresponding to *aa* and *bb* would have different coefficients.

39. Derive an expression for the normalisation constant N in

ANS. $N = 1/2\,(1 + S)^{1/2}$. S is the overlap integral.

Show that the normalisation factor for an *sp* hybrid wave function is $1/\sqrt{2}$.

Ligand Field Theory and Intermolecular Forces

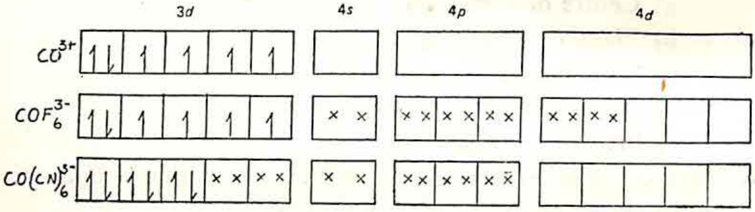
1. What do you understand by:
   a) Centre of symmetry,
   b) Plane of symmetry,
   c) Character table,
   d) Identity, and
   e) Property of a group.
2. How can you write down the orbitals for a linear diatomic molecule on the basis of group theory?
3. Discuss the application of group theory to quantum mechanics by taking a specific example.
4. List and discuss the symmetry elements possessed by the following molecules.
5. Which of the following molecules have a centre of symmetry
   1) C_6H_6, H_2O, BCl_3, $CHCl_3$,
   2) List the symmetry elements of the above molecule,
   3) Write down the multiplication table for above,
   4) Write down the result of the symmetry operation on the *p* orbitals of sulphur atom.
6. Discuss the quantum mechanics of:
   1) Weak field complexes,
   2) Strong field complexes,
   3) Sandwitch compounds.
7. What are van der Waals forces. Discuss their origin and give an outline of the quantum mechanical derivation of attraction energy.
8. Discuss the quantum mechanical treatment of:
   1) van der Waals forces,

   2) Donor-acceptor interaction,
   3) Hydrogen bond interaction.

9. Give an outline of ligand field theory based on symmetry considerations. What is the basic difference between
   a) Weak field complexes, and
   b) Strong field complexės from quantum mechanical new put.

10. The ligands F^- and CN^- are quite different in their abilities to form labile and inert complexes. F^- is a weak ligand while CN^- is a strong ligand forming outer- and inner-orbital complexes respectively. Prepare a diagram showing the configuration of COF_6^{3-} and $CO\,(CN)_6^{3-}$ and predict the number of unpaired electrons.

Solution



11. As in question 10, predict the number of unpaired electrons in

$$Fe^{3+}, \quad FeF_6^{3-} \quad Fe\,(CN)_6^{3-1}$$

ANS. 5, 5, 1.

12. By how many times the van der Waal's attraction energy would be increased when the inter nuclear distance is reduced by 1/2. ANS. 64

Compare it with the coulombs energy between two point charges when the distance between them is reduced by 1/2.

(ANS. van der Waals forces will increase 64 times and coulomb forces 4 times).

13. Show that the frequency of a charge transfer band would increase for a charge transfer complex (i) when the ionisation potential of donor increases, and (ii) when the electron-electron affinity of the acceptor decreases.

Hint :

$$h\nu_{C.T} = I\,(\nu) - A\,(A) + Q.$$

Miscellaneous

1. What is understood by tunnel effect? How does a free particle in one-dimensional box and a particle moving through an energy barrier differ energetically? Using quantum mechanical arguments obtain an expression for this probability of the particle crossing this energy barrier.
2. What do you understand by harmonic oscillator? Obtain the appropriate Schrödinger equation for this case. Give the outline of the solution and discuss the results.

APPENDIX I: SOME PHYSICAL CONSTANTS AND DEFINED VALUES

Velocity of light	c	2.997925×10^{10} cm sec^{-1}
Avogadro's number	N	6.0225×10^{23} particles mole^{-1}
Planck constant	h	6.6256×10^{-27} erg oec.
Rydberg constant for hydrogen		109,737.31 cm^{-1}
Gas constant	R	0.082054 litre-atm deg^{-1} mole^{-1} 8.3143 joules deg^{-1} mole^{-1} 1.9872 cal deg^{-1} mole^{-1}
Electron charge	e	1.60210×10^{-19} coulomb 4.80298×10^{-10} e.s.u.
Electron rest mass	e	9.1091×10^{-28} g 0.00055 a.m.u.
Proton rest mass	p	1.6725×10^{-24} g 1.007277 a.m.u.
Neutron rest mass	n	1.6748×10^{-24} g 1.008665 a.m.u.
Metre	m	1,650, 763.73 wavelengths in vacuo of the $2p^{10}$-$3d^{5}$ transition in Kr^{36}
Kilogramme	kg	mass of international kilogramme serves, France.
Second	Sec	1/31, 556, 925, 9746 of tropical year 1900
Standard gravity	g	980.67 cm sec^{-2}
Standard molar gas volume		22.412 litres
Absolute ice point	0°c.	273.15°K
Triple point of water		273.16°K

APPENDIX II: CONVERSION FACTORS

1 Faraday = 96, 487 coulombs mole^{-1}
1 Coulomb = 6.281×10^{18} electronic charges
1 Electron Volt = 1.602×10^{-12} erg
= 3.827×10^{-20} Cal
1 Metre = 39.37 inches
1 Angstrom unit = 1×10^{-8} cm
1 Litre = 1.0567 quarts
1 Kilogramme = 2.205 pounds
1 Litre-atmosphere = 24.21 Calories
= 9.89×10^{-3} joules
1 Calorie (gram) = 4.184 joules
= 2.613×10^{19} electron Volts
0°K = −273.15°C (273.16° below triple point of H_2O)
1 Atmosphere = 760 torr
= 1.013×10^{6} dynes cm^{-2}
1 Torr = 1 mm Hg at 0°C.

Further Reading

1. Taylor, T.G. Quantum Mechanics: An Introduction—George Allen and Unwin Ltd. London, 1970.
2. Kauzmann, W. Quantum Chemistry: An Introduction—Academic Press, Inc. Publishers, N.Y., 1957.
3. Pitzer, K.S. Quantum Chemistry—Prentice-Hall Inc., Englewood Cliffs, N.J. 1961.
4. Kemble, E.C. The Fundamental Principles of Quantum Mechanics, with Elementary Applications—Dover Publications Inc. New York 1958.
5. Glasstone, S. Theoretical Chemistry—D. Van Nostrand Company Inc. Princeton, New Jersey, 1961.
6. Ziock, K. Basic Quantum Mechanics—John Wiley and Sons Inc. N.Y. 1969.
7. Atkins, P.W. Molecular Quantum Mechanics Pt. III—Clarendon Press Oxford, 1970.
8. Pauling, L. and Wilson, E.B. Introduction to Quantum Mechanics—McGraw-Hill Book Co. Inc. 1935.
9. Anderson, J.M. Introduction to Quantum Chemistry—W.A. Benjamin Inc. N.Y. 1969.
10. Atkins, P.W. Molecular Quantum Mechanics Pt. I and II—Clarendon Press, Oxford, 1970.
11. Dandel, R. Quantum Chemistry, Methods and Applications—R. Lefebore Inter Science Publishers, Inc. New York 1959.
12. Mathews, P.T. Introduction to Quantum Mechanics—McGraw-Hill, London, 1968.
13. Schiff, L.T. Quantum Mechanics—McGraw-Hill Book Co. Inc. N.Y. 1955.
14. Eyring, H., Walter, J. and Kimball, G.E. Quantum Chemis-

try—John Wiley and Sons Inc. N.Y. 1944.

15. Riggs, N.V. Quantum Chemistry, Elementary Principles and Methods—McMilton Company, Collier, McMillan, Canada Ltd. Toronto, Ontario, 1969.
16. Sherwin, C.W. Introduction to Quantum Mechanics—Holt, Rinehart and Winston, N.Y. 1960.
17. Linnett, J.W. Wave Mechanics and Valency—London Methuen and Co. Ltd. N.Y. 1960.
18. Woodward, R.D. and Hoffmann, R. The Conservation of Orbital Symmetry—Verlag Chemie Gmbff, Academic Press. Inc. 1971.
19. Sching Holt, J.C. Introduction to Quantum Chemistry—Rinehart and Winston Inc. U.S.A. 1972.
20. Urch, D.S. Orbitals and Symmetry—Penguin Books Limited, Harmondsworth, Middlesex, England, 1970.
21. Schlafer, H.L. and Gleiman. Basic Principles of Ligand Field Theories—Wiley Inter Science, 1969.
22. Murrell, J.N., Kettle, S.F.A. and Tedder, J.M. Valency Theory—John Wiley and Sons Ltd. 1970.

Subject Index

Angular momentum 8
Axis of symmetry 112

Black body radiation 11
Benzene 131, 138
Boltzmann distribution law 5
Born-Oppenheimer
  approximation 87
Bound electrons 53
Butadiene 125, 137

Carotene 49
Centre of symmetry 113
Chemical bonding 92
Complex Inorganic Compounds 156
Compton effect 17
Contour diagrams 64
Crystal field theory 157

Determinants 185
Donor acceptor interaction 173
Dual nature of electron 20
Dulong and Petit low 4

Eigen value 35
Einstein equation 18, 20
Electron cloud 30
Electron repulsion theory 109
Electronic spectra of transition
  metal complexes 169
Energy of molecular orbitals 96
Ethylene 121, 138, 140
Excited states of H_2^+ 86
Exclusion principle 2

Free electron in a box 137
Free electron model 48
Free electron moving in a
  periodic potential 52
Free valence 142

Group theory 114
Group theory applied to simple
  molecules 117

Hamiltonian operator 28
Hartree self-consistent
  field method 75
Helium atom 68
Homonuclear diatomic molecules 98
Hydrogen molecule 87
Hydrogen molecule ion 78
Hyperpolarisability 36

Inclastic collision 2
Ionisation potential 9, 11

Laplacian operator 28
Large organic molecules 120
Legendre function 58
Ligand field theory 163
Linear combination of atomic
  orbitals 33
London dispersion forces 36
London interaction 170

Matrices 191
Maxwell-Boltzmann Statistics 184
M.O. theory 177

M.O. theory of large molecules 147
M.O. treatment of
  complex ions 158
Molecular orbitals of metal
  ligand bonds 161
M.O. treatment of Naphthalene 143

Normalisation constant 31, 44

Operator 194
Orthogonality theorem 34

Particle in a rectangular box 40
Particle in a ring 42
Particle on the surface of
  a sphere 46
Particle in a three
  dimensional box 40
Perturbation method 35, 69
Perturbation theory 2
Photoelectric effect 2, 15, 16
Photoelectron spectroscopy 10, 11
Planck's constant 6, 17
Plane of symmetry 113
Polyelectronic atoms 68, 77
Probability density 40

Quantum effects in kinetic
  theory 180
Quantum statistics 186

Resonance potential 9

Schrödinger wave equation 26, 28, 37
Simple Hückel M.O. theory 151
Slater orbitals 74
Small inorganic molecules 98
Specific heat of solids 3
Specific heat of diamond 3
Spherical hormonics 57
Spin pairing and chemical bond 94
Symmetry of molecules 111
Symmetry operation of orbitals 117

Tunnel effect 59

Uncertainty principle 2, 20, 21, 25

Valence bond theory 158, 176
Valence bond treatment 89
Variation method 34, 71

Weak chemical interaction 170
Wien's equation 13

ERRATA

Page	*Line*	*Present*	*Corrected*
11	35	strongly	more strongly
17	8	V^2	v^2
21	12	Wavelength, m	Wavelength, $\mathrm{m} \times 10^6$
24	33	$(mv_x \, \Delta v_x)$	$\left(m.\,\Delta v_x.\,\frac{\Delta x}{\Delta t}\right).\,\Delta t$
32	29	$\psi_b^{(2)}$	$\psi_b^{(1)}$
33	3	$\psi_b^{(2)}$	$\psi_b^{(1)}$
33	17	Eectrons	atomic orbitals
34	9	$0 + 0$	$2C_1.\,C_2S$
34	10	Hence, . . . (3.26)	Where S is the overlap integral
34	12	(3.27)	(3.26)
34	14	$c_1^2 - c_2^2 = 0$	$c_1^2 - c_2^2 = 0$ or $c_1 = \pm\, c_2 \ldots (3.27)$
35	10	$\sum_{k=1}$	$\sum_{k=1}^{n}$
35	12	k	n
35	30	$\int \psi^{\circ *} H^{\circ} \psi \, d\tau$	$\int \psi^* H \psi \, d\tau$
36	1	$\psi^{\circ *}$	ψ^*
38	3	x^2	k^2
38	5	x^2	k^2
41	5	put	pur $\psi = f_x f_y f_z$
43	5	Three	Three-fold
44	11	N_m	N_M
44	12	N_m	N

45	23	ψ_-	ψ_+
48	11	$\sin 2\theta \sin 2\phi$	$\sin^2 \theta \sin 2\phi$
53	13	$\int_r^\infty$	$\int_\infty^r$
	last	z	Z
53	14	z	Z
53	17	z	Z
58	8	m	/m/
58	17	order	order m
59	20	f_3^2	f_3^*, f_3
59	21	the whole line	delete
62	5	n	m
73	19	$\Delta_i^2 \psi$	$\nabla_i^2 \psi$
73	20	Δ_i^2	$\nabla_i^2 \psi$
75	16	and Fock	delete
81	16	ψ_a	ψ_a^*
81	17	ψ_a	ψ_a^*
81	17	ψ_b	ψ_b^*
84	17	r_{12}	R
85	5	r	R
85	10	r	R
85	12	r	Re
88	7	Nuclei	Nucleus
88	8	Nuclei	Nucleus
88	10	Nuclei	Nucleus
90	3	E_4	E_H
90	25	$\psi_b^{(2)}$	$\psi_b^{(1)}$
90	25	$\psi_b^{(1)}$	$\psi_b^{(2)}$

93	22	Self consistent	delete
93	24	C	c
96	18	σ_{1s}	σ^*_{1s}
96	20	$\sigma 2py$	$\sigma 2p_y$
96	20	$\sigma 2p_y$	$\pi^* 2p_y$
97	16	$d-d(x)$	$d-d(s)$
103	25	this	the
103	25	nuclei	nucleus
103	26	this	the
105	5	CCl_3	CCl_4
105	13	1*s*	one *s*
105	14	electrons	orbitals
134	17	$\phi_2 = \frac{1}{\sqrt{12}}(2x_1 + x_2 + x_3 + x_4 + x_5 + x_6)$	$\phi_2 = \frac{1}{\sqrt{12}}(2x_1 + x_2 - x_3 - 2x_4 - x_5 + x_6)$
134	18	$\phi_3 = \frac{1}{\sqrt{4}}(x_2 + x_3 + x_5 - x_6)$	$\phi_3 = \frac{1}{\sqrt{4}}(x_2 + x_3 - x_5 - x_6)$
145	12	$S_4 = \frac{1}{2}(x_1 - x_7 + x_5 - x)$	$S_4 = \frac{1}{2}(x_1 - x_7 + x_5 - x_8)$
181	33	$\epsilon(r) = \epsilon^* f\left(\frac{r}{\sigma}\right)$	$\epsilon(r) = \epsilon^* f\left(\frac{r}{\sigma}\right)$
193	13	$A^t = [a_{ij}]^t = [a_{ij}]$	$A^t = [a_{ij}]^t = [a_{ji}]$
34	15, 16	From equations (3.26) and (3.28) it follows that $C_1 = C_2 = \pm\frac{1}{\sqrt{2}}$	making proper substitution in eq. (3.25) we get, $c_1^2 + c_1^2 \pm 2c_1^2 S = 1 \ \ldots$ (3.28) or $c_1 = \frac{1}{(2 \pm 2S)^{1/2}}$ ...(3.29)

100	8	Add	It has now been discovered that C_2 molecule is not paramagnetic and hence m.o. description for these molecules has been lately modified.
119	17	Add in the end	It may be pointed out that in the treatment above is orbitals of oxygen are ignored.

AN INTRODUCTION TO QUANTUM MECHANICS OF CHEMICAL SYSTEMS

The book is an introductory text at the post-graduate level. Greater emphasis has been given towards understanding of the concept rather than the detail of involved mathematics. The significant feature is the comprehensive coverage of the board spectrum of applications of Quantum Mechanics to Chemical Systems. In order to make the subject more clear, as many as 80 solved and unsolved problems have been included.

Dr. R.P. Rastogi is presently Vice-Chancellor, Banaras Hindu University and a Fellow of the Indian National Science Academy. He has made significant theoretical and experimental studies in the fields of reversible and irreversible thermodynamics, propellant chemistry and non-linear dynamics of reacting systems and has published about 300 papers in reputed international and national journals. He is the author of *An Introduction to Chemical Thermodynamics*. He is the recepient of several national awards including Khosla Award, FICCI Award and Meghnad Saha Award for his scientific contributions.

Dr. V.K. Srivastava is Reader in Physical Chemistry in the Department of Chemistry, University of Gorakhpur. His main research interest is concerned with biochemistry of Vision and Cataracts. He has written several textbooks and has published over 50 papers in international and national journals.

Rs. 49.00

OXFORD & IBH PUBLISHING CO.
NEW DELHI BOMBAY **CALCUTTA**

ISBN 81-204-0073-9